PB90-181983

Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Volume 3. Primary Copper Smelting, Primary Electrolytic Copper Refining, Secondary Copper Metallurgical Acid Plants

(U.S.) Environmental Protection Agency, Washington, DC

May 89

U.S. Department of Commerce
National Technical Information Service
NTIS

BIBLIOGRAPHIC INFORMATION

PB90-181983

Report Nos: EPA/440/1-89/019.3

Title: Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Volume 3. Primary Copper Smelting, Primary Electrolytic Copper Refining, Secondary Copper, Metallurgical Acid Plants.

Date: May 89

Performing Organization: Environmental Protection Agency, Washington, DC. Industrial Technology Div.

Type of Report and Period Covered: Final rept.

Supplementary Notes: See also PB87-121752 and Volume 2, PB90-181975 and Volume 4, PB90-181991.

NTIS Field/Group Codes: 68D, 68A, 68C, 71N, 99B

Price: PC A17/MF A03

Availability: Available from the National Technical Information Service, Springfield, VA. 22161

Number of Pages: 385p

Keywords: *Water pollution control, Industrial waste treatment, Performance standards, Cost analysis, Guidelines, Smelting, Refining, Sampling, Air pollution control, Solid waste disposal, Materials recovery, Substitutes, *Best technology, *New source performance standards, *Water pollution standards, *Clean Water Act of 1977, *Nonferrous metals, *Pretreatment(Water), *Copper industries, Pollution regulations, Point sources, Technology utilization.

Abstract: Table of Contents: Subcategory profile; Subcategorization; Water use and wastewater characteristics; Selection of pollutant parameters; Control and treatment technologies; Costs, energy, and nonwater quality aspects; Best practicable technology currently available; Best available technology economically achievable; New source performance standards technical approach to BDT; Pretreatment standards; Best conventional pollution control technology.

United States
Environmental Protection
Agency

Office of Water

Office of Water Regulations
and Standards (WH-552)
Industrial Technology Division
Washington, DC 20460

EPA 440/1-89-019.3
May 1989

PB90-181383

EPA

Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category

FINAL

Volume III

Primary Copper Smelting
Primary Electrolytic Copper Refining
Secondary Copper
Metallurgical Acid Plants

[illegible]
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

Printed on Recycled Paper

ORGANIZATION OF THIS DOCUMENT

This development document for the nonferrous metals manufacturing category consists of a general development document which considers the general and overall aspects of the regulation and 31 subcategory specific supplements. These parts are organized into 10 volumes as listed below.

The information in the general document and in the supplements is organized by sections with the same type of information reported in the same section of each part. Hence to find information on any specific aspect of the category one would need only look in the same section of the general document and the specific supplements of interest.

The ten volumes contain contain the following subjects:

Volume I	General Development Document
Volume II	Bauxite Refining Primary Aluminum Smelting Secondary Aluminum Smelting
Volume III	Primary Copper Smelting Primary Electrolytic Copper Refining Secondary Copper Refining Metallurgical Acid Plants
Volume IV	Primary Zinc Primary Lead Secondary Lead Primary Antimony
Volume V	Primary Precious Metals and Mercury Secondary Precious Metals Secondary Silver Secondary Mercury
Volume VI	Primary Tungsten Secondary Tungsten and Cobalt Primary Molybdenum and Rhenium Secondary Molybdenum and Vanadium
Volume VII	Primary Beryllium Primary Nickel and Cobalt Secondary Nickel Secondary Tin
Volume VIII	Primary Columbium and Tantalum Secondary Tantalum Secondary Uranium
Volume IX	Primary and Secondary Titanium Primary Zirconium and Hafnium
Volume X	Primary and Secondary Germanium and Gallium Primary Rare Earth Metals Secondary Indium

DEVELOPMENT DOCUMENT
for
EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS
for the
NONFERROUS METALS MANUFACTURING POINT SOURCE CATEGORY

VOLUME III

Primary Copper Smelting
Primary Electrolytic Copper Refining
Secondary Copper Refining
Metallurgical Acid Plants

William K. Reilly
Administrator

Rebecca Hanmer, Acting
Assistant Administrator for Water

Martha Prothro, Director
Office of Water Regulations and Standards

Thomas P. O'Farrell, Director
Industrial Technology Division

Ernst P. Hall, P.E., Chief
Metals Industry Branch
and
Technical Project Officer

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U.S. Environmental Protection Agency
Office of Water
Office of Water Regulations and Standards
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For detailed contents see detailed contents list in individual supplement.

NONFERROUS METALS MANUFACTURING POINT SOURCE CATEGORY

DEVELOPMENT DOCUMENT SUPPLEMENT

for the

Primary Copper Smelting Subcategory

William K. Reilly
Administrator

Rebecca Hanmer
Acting Assistant Administrator for Water

Martha Prothro, Director
Office of Water Regulations and Standards

Thomas P. O'Farrell, Director
Industrial Technology Division

Ernst P. Hall, P.E., Chief
Metals Industry Branch
and
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SECTION I

SUMMARY

On February 27, 1975 (40 FR 8514), EPA promulgated interim technology-based effluent limitations for existing sources and proposed new source performance and pretreatment standards for the primary copper subcategory of the nonferrous metals manufacturing point source category. These effluent guidelines and standards limited the quantities of total suspended solids, copper, cadmium, lead, zinc, and pH in primary copper subcategory wastewaters.

The 1975 BPT limitations for primary copper smelters, and primary copper refiners located on-site with smelters, required no discharge of process wastewater pollutants with two rainfall related exceptions. When a 10-year, 24-hour rainfall event occurred, primary copper smelters were allowed to discharge a volume of water equal to that resulting from the 10-year, 24-hour rainfall event falling within a smelter's wastewater impoundment. Additionally, smelters were allowed to discharge a volume of water equal to that resulting from the difference between monthly evaporation and precipitation. This discharge was subject to concentration-based limitations.

The 1975 BAT regulation for primary copper smelters allowed a discharge of water equal to the 25-year, 24-hour rainfall event falling within a smelter's wastewater impoundment. This discharge was subject to no effluent standards. Additionally, smelters were allowed to discharge a volume of water equal to that resulting from the difference between the net monthly evaporation and net monthly precipitation. This discharge was subject to concentration-based limitations.

Revised BPT limitations were issued for the primary copper subcategory on July 2, 1980 (45 FR 44926). The Agency retained the no discharge of process wastewater pollutants requirement for primary copper smelters and the 10-year, 24-hour storm event discharge provision. The monthly discharge allowance for smelters when the net precipitation was greater than the net evaporation was deleted.

In the March 8, 1984 rulemaking (49 FR 8742), EPA promulgated modifications to BAT, NSPS, and PSNS for this subcategory pursuant to the provisions of Sections 301, 304, 306, and 307 of the Clean Water Act, as amended. This supplement provides a compilation and analysis of the background material used to develop these effluent limitations and standards. The BPT limitations promulgated in 1980 remain unchanged and are discussed later for information purposes only.

The primary copper smelting subcategory is comprised of 19 plants. Of the 19 plants, one discharges directly to rivers, lakes, or streams; none discharge indirectly through publicly owned treatment works (POTW); and 18 achieve zero discharge of process wastewater.

For the primary copper smelting subcategory, promulgated BAT effluent limitations do not allow a discharge of process wastewater pollutants except for the 25-year, 24-hour rainfall event exemption. NSPS and PSNS also do not allow a discharge of process wastewater pollutants. There are no storm water discharge exemptions provided for new sources.

SECTION II

CONCLUSIONS

In the 1980 rulemaking, EPA divided primary copper production into two subcategories: the primary copper smelting subcategory and the primary electrolytic copper refining subcategory. This subcategorization has been retained for the primary production of copper and the primary copper smelting subcategory has not been further subdivided into segments or building blocks for the purpose of regulation.

EPA promulgated BPT effluent limitations for the primary copper smelting subcategory on July 2, 1980 as Subpart D of 40 CFR Part 421. No modifications are promulgated for the 1980 BPT. The promulgated BPT for the primary copper smelting subcategory is no discharge of process wastewater pollutants, subject to an uncontrolled discharge equal to the volume in excess of storm water from a 10-year, 24-hour storm falling on a cooling impoundment.

EPA has amended BAT effluent limitations for the primary copper smelting subcategory. EPA promulgated BAT for the primary copper smelting subcategory be no discharge of process wastewater pollutants, subject to an uncontrolled discharge equal to the volume of storm water in excess of a 25-year, 24-hour storm falling on a cooling impoundment.

EPA promulgated NSPS for the primary copper smelting subcategory be no discharge of process wastewater pollutants with no provision for a storm water discharge allowance.

EPA did not promulgate pretreatment standards for existing sources (PSES) for the primary copper smelting subcategory, because there are no existing indirect dischargers in this subcategory.

EPA promulgated PSNS for the primary copper smelting subcategory be no discharge of process wastewater pollutants with no provision for a storm water discharge allowance.

SECTION III

SUBCATEGORY PROFILE

This section of the primary copper smelting supplement describes the raw materials and processes used in smelting pure copper from copper bearing ores to pure copper and presents a profile of the primary copper smelting plants identified in this study.

DESCRIPTION OF PRIMARY COPPER PRODUCTION

The manufacturing of copper from copper sulfides through pyrometallurgical processes may consist of seven steps:

1. Roasting,
2. Smelting,
3. Leaching, if preceded by a pyrometallurgical step,
4. Converting,
5. Fire refining,
6. Slag granulation and dumping, and
7. Casting of products from these operations.

In actual practice, however, not all of these operations are practiced at all smelters and they may be combined in several ways with other processes such as electrolytic refining and metallurgical acid production. Figure III-1 (page 1045) illustrates the copper smelting process. Electrolytic refining and product casting, as well as recovery of precious metals from anode slimes, are discussed in the Primary Electrolytic Copper Refining Subcategory Supplement.

RAW MATERIALS

There are approximately 160 known copper minerals, about a dozen of which are commercially important. The most important copper ores in the United States are chalcopyrite, chalcocite, covellite, chrysocolla, bornite, cuprite, and malachite. These are either sulfide, silicate, or oxide ores. Most of the copper ore processed in the United States is a copper sulfide. At the mine site, copper bearing ore is concentrated into copper sulfide which forms the main raw material for copper smelting.

ROASTING

Roasting, the first step in producing copper from copper sulfide concentrates, oxidizes the iron sulfide present in the copper concentrate to iron oxide and SO_2 gas. During this oxidation process, the amount of air added is limited so as not to oxidize the copper sulfide.

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Keeping the copper sulfide unoxidized allows for easy removal of the iron oxide during smelting because of specific gravity differences between iron oxide and copper sulfide.

Depending on the raw material and the type of smelting furnace, copper sulfide concentrates may be roasted in one of three ways: multiple-hearth roasters, fluidized bed roasters, and sintering machines. Multiple-hearth roasters, as the name suggests, contain several hearths where the concentrate is roasted. A fluidized bed roaster suspends concentrate in air while the roasting takes place. The fluidized bed roaster has replaced many multiple-hearth roasters because its capacity is roughly eight times greater than a multiple-hearth roaster. A third method of roasting, known as sintering, actually melts the surface of the concentrate. After the calcine (the roasted product) cools, the concentrate has become agglomerated and is fed to a blast furnace. Currently there are no blast furnaces used in the United States primary copper smelting plants.

The SO_2 gasses and particulate matter produced during roasting are collected in a centralized flue. Of the seven primary copper smelters who reported sufficient information about roasting, one uses a dry control method, one uses a wet scrubber, and five have no roasting air pollution control for particulate matter. Traditionally, control of SO_2 emissions are accomplished with an acid plant. By definition this waste stream becomes part of the metallurgical acid plant subcategory, and is further considered in the Metallurgical Acid Plant Supplement.

SMELTING

The calcine produced from roasting is composed primarily of copper sulfide and iron oxide. With the aid of a fluxing agent, the calcine is melted in a smelting furnace. Through gravity separation, the copper sulfide is separated from the iron oxide. The iron oxide and fluxing agents float to the top of the bath, forming slag, which is continuously tapped from the furnace. The copper sulfide and other heavy metals settle to the bottom of the furnace and are periodically tapped. The matte, or molten metal from the furnace bottom, is composed of copper, nickel, iron, cobalt, sulfur, and small amounts of precious metals. The purity of the matte can be improved by altering both the roasting and smelting processes. However, optimum conditions dictate that the matte contain approximately 35 percent iron because, as iron oxide concentrations are reduced, more copper is removed with the slag.

Three types of furnaces may be used to smelt roasted calcines: reverberatory, electric, and blast furnaces. The most widely used of the three, the reverberatory furnace, was designed to process fine concentrate. A reverberatory furnace is characterized by a low roof with heat added by burning fuel oil, natural gas, or pulverized coal between the charge and the roof. An electric furnace send an electric current through the charge melting it with the heat liberated through electrical resistance.

The major advantage of an electric furnace over a reverberatory furnace is that the volume of off-gases is reduced. With a smaller volume of gas, the SO_2 content is higher, thus the SO_2 is more readily recoverable in an acid plant.

Several variations of the preceding smelting process description have been developed; they include the Mitsubishi and Noranda processes and the smelting of unroasted calcines. Continuous matte smelting and converting furnaces, known as the Mitsubishi process, incorporate three furnaces to combine roasting, smelting, and converting (oxidation of copper sulfide) into one continuous process. By combining these three processes, smelting rates and heating costs are greatly reduced. The Noranda process, sometimes referred to as Smelting-Converting Reactions, combines the smelting and converting processes together. The reactions that take place within the reactor are similar to those that occur during a normal two-stage smelting and converting process. Iron contained within the charge is first oxidized followed by oxidation of the copper sulfide.

Wastewater generated from smelting is attributable to control of air pollution and slag granulation. Of the 19 copper smelters in the United States reporting data, one plant controls air pollution with a wet scrubber, five use dry control methods, and six report no control of air pollution.

Slag tapped from the smelting furnace is granulated with water jets to ease handling and disposal problems. An alternative to slag granulation is slag dumping. With slag dumping, the molten slag is dumped onto the ground (slag pile) and allowed to air cool. This process is also termed "pancaking." In granulation, the slag is taken to the slag disposal area in its molten form and is impacted by a high velocity jet of water. The resultant waste material is finely divided and is either stored as waste or sold as road bedding or concrete agglomerate. With only three plants reporting slag granulation, it is apparent the preferred method of slag disposal is slag dumping. There are three copper smelters who reported practicing slag granulation.

CONVERTING

The composition of the matte from the smelting process is primarily copper sulfide and iron sulfide. To form blister copper (98 percent pure copper), the matte undergoes a two-stage process. Compressed air is blown into the matte converting the remaining iron sulfide to iron oxide. Silica is added to form iron silicate which floats to the top as slag:

$$2FeS + 3O_2 + SiO_2 \text{ ----> } 2FeO \cdot SiO_2 + 2SO_2$$

After skimming the slag, additional compressed air is added to oxidize the copper sulfide to copper and SO_2:

$$Cu_2S + O_2 \text{ ----> } 2Cu + SO_2$$

The remaining metal is now 98 percent pure copper. This product is commonly referred to by industry as "blister copper."

The SO_2 emissions and particulate matter leaving the furnace are captured with air scrubbers and the particulate returned to the smelter. The slag removed during conversion contains a relatively large amount of copper and is returned to the smelter.

Of the 19 copper smelters, 13 use a conversion process. Two of these plants use wet scrubbers, eight use dry air pollution control methods and four reported no control (one plant did not provide this data). The two plants that use wet air pollution control use it as a method for pretreatment before the gas enters an acid plant. The scrubber liquor cools and humidifies the gas along with removing particulate matter. Wastewater from these scrubbers, therefore, is considered a part of the metallurgical acid plant subcategory.

FIRE REFINING

After the converting process is completed, further purification of the copper is required to improve certain physical properties such as ductility and conductivity. The first stage of the refining process is commonly called fire refining and is normally conducted at the smelting site. Impurities within the copper other than precious metals have a higher affinity for oxygen than copper. Compressed air is blown into the molten bath to oxidize the impurities which are removed as slag with the help of a fluxing agent and returned to the smelter. After several cycles of oxidation and slag removal, the bath becomes saturated with copper oxide. The molten bath is then converted back to copper by adding reducing agents such as green wood poles, natural gas, or ammonia. Copper leaving this process usually contains 0.1 to 0.3 percent oxygen.

Currently in the United States, there is no wastewater generated from any fire refining process. There were seven facilities that reported using fire refining methods. Of these seven smelters, three reported using dry methods to control air emissions.

CASTING

The final step in the smelting process is casting the fire refined or blister copper into solid shapes. Most usually this is into the shape of an anode for further refining in an electrolytic process. The casting of blister copper was found, during the study for the 1980 rulemaking to be accomplished without the generation and discharge of process wastewater.

SUMMARY OF WASTEWATER SOURCES

In summary, the principal uses of water in the primary copper smelting subcategory are due to smelting wet air pollution control and slag granulation. There are other minor wastewater streams associated with primary copper smelting. These wastewater streams include, but are not limited to, maintenance and cleanup water and storm water runoff. These wastewater streams are not considered as a part of this rulemaking. EPA believes the flows and pollutant loadings associated with these waste streams are insignificant relative to the waste streams selected and are best handled by the appropriate permit authority on a case-by-case basis under the authority of Section 402 of the Clean Water Act.

AGE, PRODUCTION, AND PROCESS PROFILE

The primary copper smelting subcategory consists of 19 operations. The location and discharge status of the primary copper smelters in the United States at the time of the survey is shown in Figure III-2 (page 1046). In some cases both smelting and refining operations are found at or near the same site. As a rule, however, smelters are located near copper mines and mills in the Southwest, and electrolytic refineries are either found near smelters or near maritime centers.

Table III-1 (page 1042) shows the average age of the smelters as approximately 40 years. As seen in Table III-2 (page 1043), the average smelter plant production is approximately 200,000 tons per year of smelted copper.

As shown in Table III-1, only one of the 19 copper smelters discharges wastewater. This facility is a direct discharger Table III-3 (page 1044) presents a summary of the number of facilities with a reported process and the number of facilities generating wastewater within that process.

TABLE III-1

INITIAL OPERATING YEARS (RANGE)
SUMMARY OF PLANTS IN THE PRIMARY COPPER SMELTING SUBCATEGORY BY DISCHARGE TYPE

	Primary Copper Smelting Plant Age Range (Years)									
	1983- 1973	1972- 1968	1967- 1958	1957- 1948	1947- 1938	1937- 1918	1917- 1903	Before 1903		
Discharge Type	0-10	10-15	15-25	25-35	35-45	45-65	65-80	80- +	NR	Total
Direct	-	-	-	-	-	-	1	-	-	1
Zero	1	1	2	4	-	1	5	-	4	18
Total	1	1	2	4	0	1	6	0	4	19

TABLE III-2

PRODUCTION RANGES FOR PRIMARY COPPER SMELTING PLANTS

(tons/yr)

Production (1976) Range	Number of Copper Smelters
0 - 50000	5
50000 - 100000	3
100000 - 150000	4
150000 - 200000	2
200000 - Above	3
NR	2
TOTAL PLANTS	19

TABLE III-3

PRIMARY COPPER SMELTING SUBCATEGORY SUMMARY OF PROCESSES AND ASSSOCIATED WASTE STREAMS

Process	No. of Plants With Process	No. of Plants Reporting Generating Wastewater*
Roasting	8	1
Smelting	15	4
Converting	14	1
Fire Refining	7	0

* Through reuse or evaporation practices, a plant may generate a wastewater from a particular process but not discharge it.

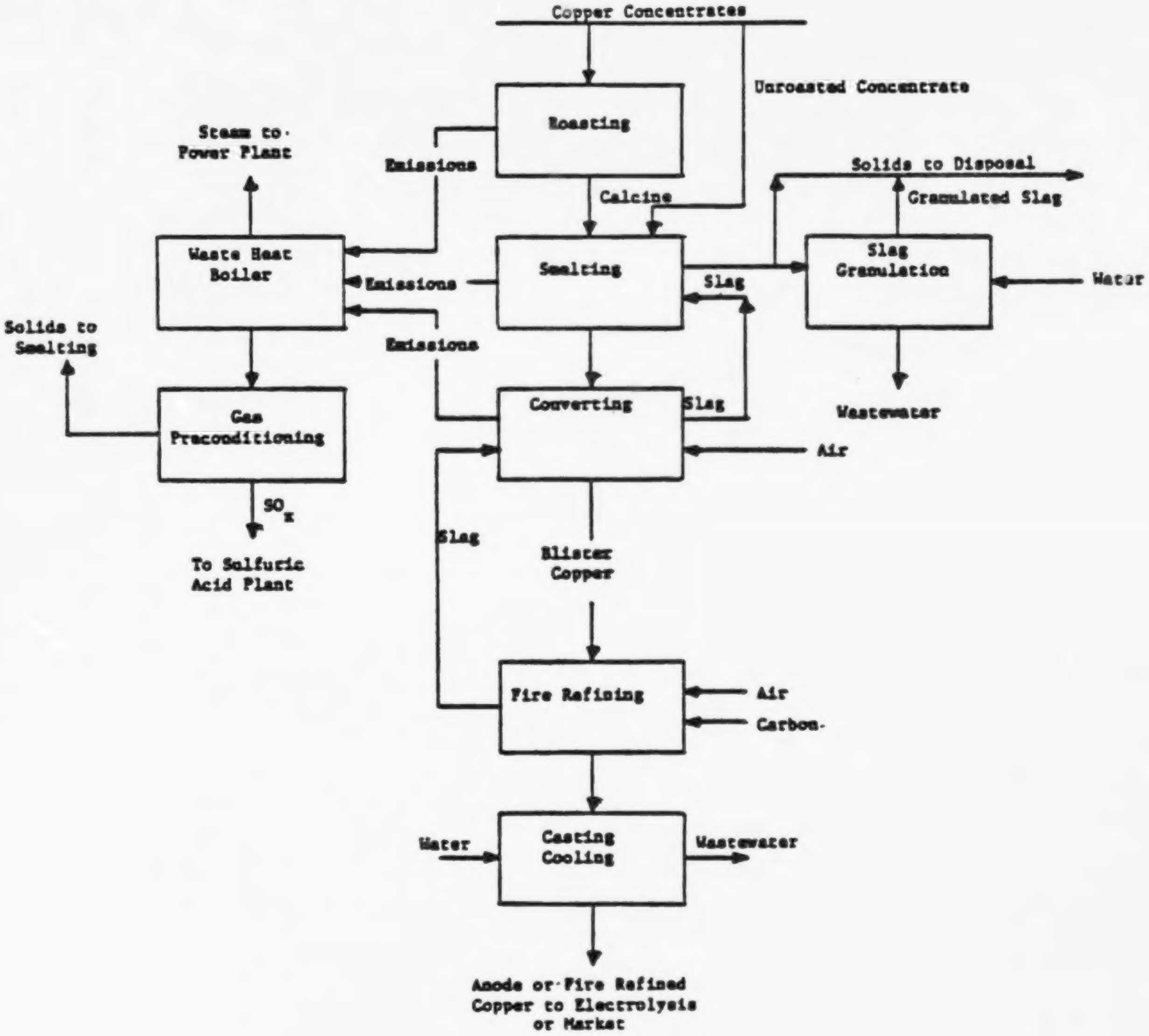
Copper Concentrates
Unroasted Concentrate
Roasting
Steam to Power Plant
Emissions
Calcine
Solids to Disposal
Granulated Slag
Waste Heat Boiler
Emissions
Smelting
Slag
Slag Granulation
Water
Solids to Smelting
Emissions
Converting
Slag
Wastewater
Gas Preconditioning
Air
SO$_x$
To Sulfuric Acid Plant
Slag
Blister Copper
Fire Refining
Air
Carbon
Water
Casting Cooling
Wastewater
Anode or Fire Refined Copper to Electrolysis or Market

FIGURE III-1
PRIMARY COPPER SMELTING PROCESS

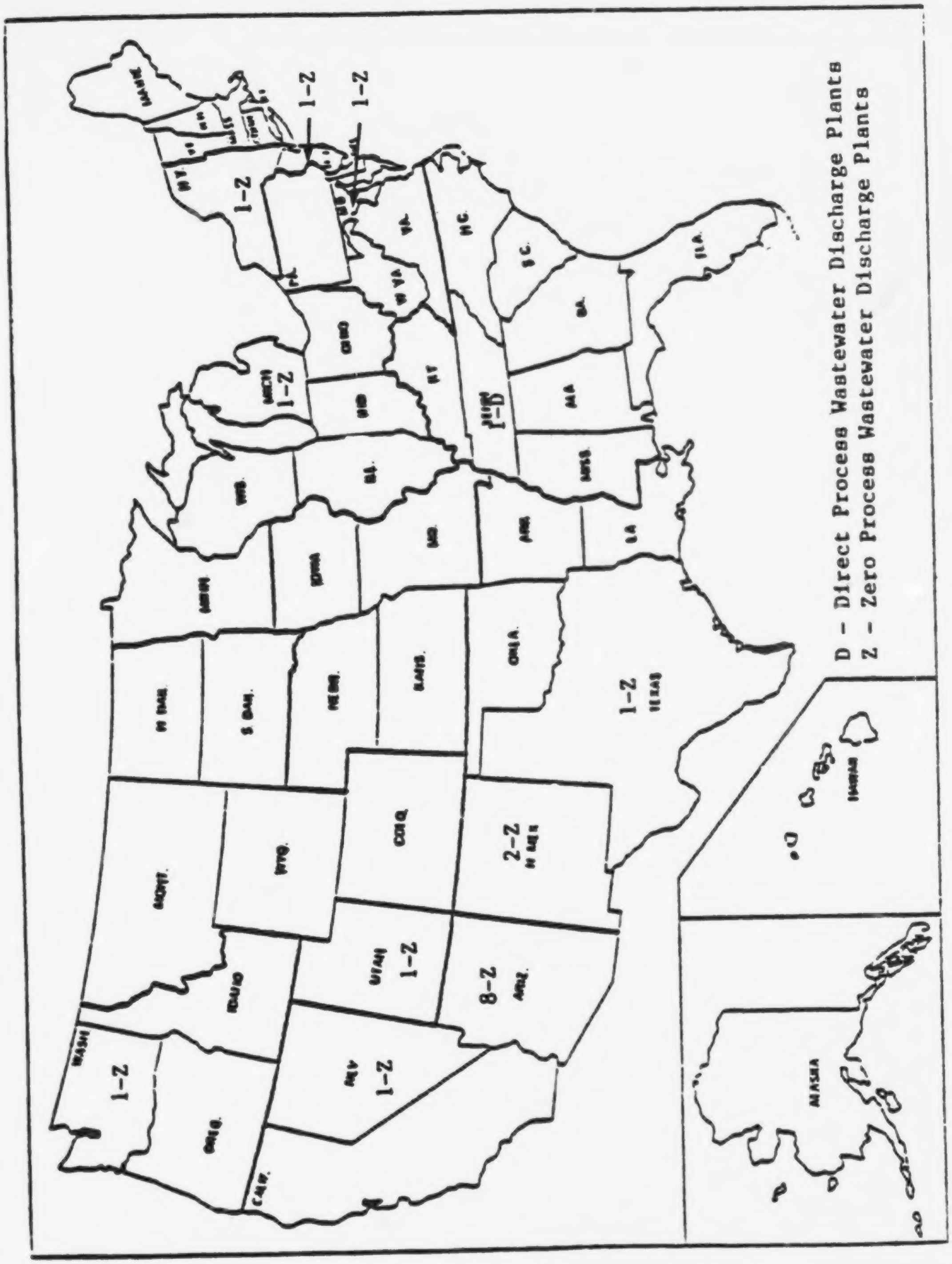
D - Direct Process Wastewater Discharge Plants
Z - Zero Process Wastewater Discharge Plants
1-Z
1-Z
1-Z
1-Z
MICH
1-D
TENN
1-Z
TEXAS
2-Z
N MEX
1-Z
UTAH
8-Z
ARIZ
1-Z
WASH
1-Z
NV
ALASKA
HAWAII

FIGURE III-2

GEOGRAPHIC LOCATIONS OF PRIMARY COPPER SMELTING PLANTS

SECTION IV

SUBCATEGORIZATION

This section summarizes the factors considered during the designation of the primary copper smelting subcategory.

Primary electrolytic copper refiners located onsite with primary copper smelters were considered as a single subcategory during the previous 1975 rulemaking. Primary copper refiners not located on site with smelters were considered as a separate subcategory. The 1975 rulemaking established interim BPT and BAT limitations, along with NSPS and PSNS for primary copper. In 1980, a modified BPT regulation was promulgated for primary copper operations that divided primary copper into smelting and refining operations regardless of location or association with other operations.

FACTORS CONSIDERED IN DESIGNATING THE PRIMARY COPPER SMELTING SUBCATEGORY

The factors listed for general subcategorization were each evaluated when considering subdivision of the primary copper smelting subcategory. Three factors were particularly important in establishing the primary copper smelting subcategory; the type of metal produced, the nature of the raw materials used, and the manufacturing processes employed. Analysis of these three factors, along with other considerations discussed below, resulted in the designation of the primary copper smelting subcategory.

Raw Materials

The raw materials usually used for primary copper smelting are copper ores and in the United States sulfide ores are used exclusively for smelting. The raw materials for electrolytic refining are either blister copper produced by fire refining or extracted copper from leaching and related mining. These raw materials are obviously quite different and do not appear to permit continued consolidation of smelting and refining.

Type of Metal Produced

Copper smelting with fire refining produces a somewhat impure copper (98+% Copper) which must be further refined for most uses while electrolytic refining produces a high purity copper (99.9+% copper) which can be used for most purposes without further refining or alloying. Hence there is no indication from the products manufactured that the segments should be co-regulated.

Manufacturing Processes Employed

The operations involved in copper smelting genera;y produce off-gasses which are rich in sulfur dioxide (SO2) and which must be further treated before release to the atmosphere. This is usually accomplished by the installation of a sulfuric acid plant on the exhaust gas system from the smelter. Off-gasses from the electrolytic refining operations are not as rich in sulfur compounds and cannot be treated to control air pollution in a sulfuric acid plant. This difference in the waste products from the smelting and the electrolytic refining operations is quite significant and forms a rational basis for separating the operations into separate subcategories.

During the study for the 1980 BPT rulemaking, the ability of the primary copper smelting processes to consume water and not require a discharge was extensively studied. This study concluded that the principal sources of wastewater in the subcategory are smelting, slag granulation and casting and that all of these wastewaters can be totally recycled and reused.

By definition, the gas conditioning and cleansing which must be done on smelter gasses before injecting them into the sulfuric acid plant is part of the acid plant subcategory operations. Because of this separation the primary smelting operations can be operated without the need to discharge wastewater from the operations. The electrolytic refining operations on the other hand cannot be operated without the discharge of water from the processes.

PRODUCTION NORMALIZING PARAMETERS

Effluent limitations and standards for primary copper smelting operations are based on no discharge of process wastewater pollutants. No subdivisions or building blocks are being provided for discharge allowances in this subcategory. Therefore, no production normalizing parameters (PNP) are presented for this category.

SECTION V

WATER USE AND WASTEWATER CHARACTERISTICS

This section describes the characteristics of wastewater associated with the primary copper smelting subcategory. Data used to quantify wastewater flow and pollutant concentrations are presented, summarized, and discussed. The contribution of specific production processes to the overall wastewater discharge from primary copper smelting plants is identified whenever possible.

Two principal data sources were used in the development of effluent limitations and standards for this subcategory: data collection portfolios and field sampling results. Data collection portfolios, completed for the primary copper smelting subcategory, contain information regarding wastewater flows and production levels.

Since the data collection portfolios were collected, the Agency received updated and revised flow and production for some waste streams through comments on the proposed regulation and through special requests. These data are also included in this section.

In order to quantify the pollutant discharge from primary copper smelting plants, a field sampling program was conducted. Wastewater samples were collected in two phases: screening and verification. The first phase, screen sampling, was to identify which toxic pollutants were present in the wastewaters from production of the various metals. Screening samples were analyzed for 125 of the 126 toxic pollutants and other pollutants deemed appropriate. Because the analytical standard for TCDD was judged to be too hazardous to be made generally available, samples were never analyzed for this pollutant. There is no reason to expect that TCDD would be present in primary copper smelting wastewater. A total of 10 plants was selected for screen sampling in the nonferrous metals manufacturing category. A complete list of the pollutants considered and a summary of the techniques used in sampling and laboratory analyses are included in Section V of Vol. I. In general, the samples were analyzed for three classes of pollutants: toxic organic pollutants, toxic metal pollutants, and criteria pollutants (which includes both conventional and nonconventional pollutants).

As described in Section IV of this supplement, primary copper smelting has been further categorized into three subdivisions. This regulation contains zero discharge limitations and standards for three unit processes generating process wastewater. Differences in the wastewater characteristics associated with these subdivisions are to be expected. For this reason, wastewater streams corresponding to each subdivision are addressed separately in the discussions that follow.

WASTEWATER SOURCES, DISCHARGE RATES, AND CHARACTERISTICS

The wastewater data presented in this section were evaluated in light of production process information compiled during this study. As a result, it was possible to identify the principle wastewater sources in the primary copper smelting subcategory:

1. Smelting wet air pollution control,
2. Slag granulation, and
3. Anode casting contact cooling.

Data supplied by dcp responses were used to calculate the amount of water used per metric ton of production. Water use (application rate) is defined as the volume of water or other fluid required for a given process per mass of copper product and is therefore based on the sum of recycle and make-up flows to a given process. Wastewater flow discharged after pretreatment or recycle (if these are present) is used in calculating the production normalized flow--the volume of wastewater, discharged from a given process to further treatment, disposal, or discharge per mass of copper produced. Differences between the water use and wastewater flows associated with a given stream result from recycle, evaporation, and carry-over on the product. The production values used in calculations correspond to the production normalizing parameter, PNP, assigned to each stream, as outlined in Section IV. There are no PNPs for the primary copper smelting subcategory because no discharge allowances have been provided for any specific process or building block. Production normalized flows are compiled and statistically analyzed by stream type. Where appropriate, an attempt is made to identify factors that could account for variations in water use. This information is summarized in this section.

Characteristics of wastewater from the previously listed processes were determined from sampling data collected at primary copper smelters. This data was used to determine the pollutants present in each waste stream, and to estimate the yearly mass of pollutant generated by each waste stream for the entire industry. There were site visits at three smelters which represents 16 percent of the smelters. Diagrams indicating the sampling sites and contributing production processes are shown in Figures V-1 to V-3 (pages 1063 - 1065).

In the data collection portfolios, plants were asked to indicate whether or not any of the toxic pollutants were believed to be present in their wastewater. Responses for the toxic metals selected as pollutant parameters are summarized below for those plants responding to that portion of the questionnaire. The tally from plants that are solely copper smelters and for plants that have both smelting and refining is shown in Table V-1 (page 1053).

These data demonstrate that the process wastewater contains quantifiable concentrations of toxic metal pollutants.

The raw wastewater sampling data for the primary copper smelting subcategory are presented in Tables V-3 and V-4 (pages 1055 and 1056). The stream codes displayed in Figures V-1 through V-3 (pages 1063 - 1065) may be used to identify the location of each of the samples. Where no data are listed for a specific day of sampling, the wastewater samples for the stream were not collected. If the analyses did not detect a pollutant in a waste stream, the pollutant was omitted from the table.

The data tables included some samples measured at concentrations considered not quantifiable. The base neutral extractable, acid extractable, and volatile toxic organics generally are considered not quantifiable at concentrations equal to or less than 0.010 mg/l. Below this concentration, organic analytical results are not quantitatively accurate; however, the analyses are useful to indicate the presence of a particular pollutant. The pesticide fraction is considered not quantifiable at concentrations equal to or less than 0.005 mg/l. Nonquantifiable results are designated in the tables with an asterisk (double asterisk for pesticides).

These detection limits shown on the data tables are not the same in all cases as the published detection limits for these pollutants by the same analytical methods. The detection limits used were reported with the analytical data and hence are the appropriate limits to apply to the data. Detection limit variation can occur as a result of a number of laboratory-specific, equipment-specific, and daily operator-specific factors. These factors can include day-to-day differences in machine calibration, variation in stock solutions, and variation in operators.

The statistical analysis of data includes some samples measured at concentrations considered not quantifiable. Data reported as an asterisk are considered as detected but below quantifiable concentrations, and a value of zero is used for averaging. Toxic organic, nonconventional, and conventional pollutant data reported with a "less than" sign are considered as detected but not further quantifiable. A value of zero is also used for averaging. If a pollutant is reported as not detected, it is excluded in calculating the average. Finally, toxic metal values reported as less than a certain value were considered as not detected and a value of zero is used in the calculation of the average. For example, three samples reported as ND, *, and 0.021 mg/l have an average value of 0.010 mg/l. The averages calculated are presented with the sampling data. These values were not used in the selection of pollutant parameters.

In the following discussion, water use and field sampling data are presented for each operation. Appropriate tubing or background blank and source water concentrations are presented with the summaries of the sampling data. Figures V-1 through V-3 show the location of wastewater sampling sites at each facility. The method by which each sample was collected is indicated by number, as follows:

1. one-time grab
2. 24-hour manual composite
3. 24-hour automatic composite
4. 48-hour manual composite
5. 48-hour automatic composite
6. 72-hour manual composite
7. 72-hour automatic composite

COPPER SMELTING WASTEWATER SOURCES AND CHARACTERISTICS

Presented below is a discussion of the characteristics of wastewater from the significant sources attributable to the smelting of copper concentrates. Wastewater generated from preconditioning of roasting and converting off-gases is considered in the Metallurgical Acid Plants Supplement.

Smelting Wet Air Pollution Control

Roasted calcines are charged to a smelting furnace for separation of copper sulfide and iron oxide. In this process fluxing agents are added to form an iron silicate slag which floats to the top of the charge and is removed. Gaseous emissions from this operation contain low SO_2 concentrations but significant amounts of particulate matter. Consequently, there were five out of six plants who reported using dry air pollution control devices. There was one facility that reported using a wet scrubber to control air emissions from its smelter and the scrubber liquor was eventually evaporated. This stream was not sampled, but based on the raw materials used and the products of the smelting process, this wastewater should contain soluble salts such as metallic sulfates, chlorides and various metals.

Slag Granulation and Casting

Disposal of smelter furnace slag is normally done through stock piling. There were three plants that reported using high pressure water jets to granulate the slag before dumping. The water usage and discharge rates at these three plants is presented in Table V-2 (page 1054). Wastewater from this operation should contain treatable concentrations of total suspended solids and dissolved toxic metal pollutants (0.40 mg/l arsenic). Table V-4 (page 1056) presents the sampling data gathered at primary copper smelters. Copper casting cooling water data is presented in table V-3 (page 1065) and copper anode casting water data is included in table V-4.

TABLE V-1

INDICATED PRESENCE OR ABSENCE OF TOXIC METAL POLLUTANTS DCP DATA

For Smelters only

	Known Present	Believed Present	Believed Absent	Known Absent
Antimony	2	3	2	0
Cadmium	4	2	1	0
Chromium	2	3	2	0
Copper	5	2	0	0
Lead	5	1	1	0
Nickel	4	2	1	0
Selenium	4	2	1	0
Zinc	5	1	1	0

For Smelters and Refiners Combined

	Known Present	Believed Present	Believed Absent	Known Absent
Antimony	4	1	2	0
Cadmium	4	1	2	0
Chromium	4	0	3	0
Copper	7	0	0	0
Lead	5	1	1	0
Nickel	4	2	1	0
Selenium	4	2	1	0
Zinc	5	2	0	0

TABLE V-2

WATER USE AND DISCHARGE RATES FOR SLAG GRANULATION

(l/kkg of copper smelted)

Plant Code	Percent Recycle	Production Normalized Water Use (l/kkg)	Production Normalized Water Use (gal/ton)	Production Normalized Discharge Flow (l/kkg)	Production Normalized Discharge Flow (gal/ton)
71*	0	89930	21520	0	0
214	80	104407	24986	20881	4997
7001	0	10056	2407	10056	2407

* - Disposal through solar evaporation.

TABLE V-3

PRIMARY COPPER SAMPLING DATA
FIRE REFINED COPPER CASTING CONTACT COOLING WATER RAW WASTEWATER

Pollutants	Stream Code	Sample Type	Source(b)	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
114. antimony	216	1		< 0.050			< 0.050
115. arsenic	216	1		< 0.002			< 0.002
117. beryllium	216	1		< 0.002			< 0.002
118. cadmium	216	1		< 0.020			< 0.020
119. chromium	216	1		< 0.024			< 0.024
120. copper	216	1		1.61			1.61
122. lead	216	1		< 0.060			< 0.060
123. mercury	216	1		< 0.0005			< 0.0005
124. nickel	216	1		< 0.005			< 0.05
125. selenium	216	1		0.015			0.015
126. silver	216	1		< 0.025			< 0.025
127. thallium	216	1		< 0.100			<0.100
128. zinc	216	1		0.052			0.052
Nonconventionals							
chemical oxygen demand (COD)	216	1		< 2			< 2
total organic carbon (TOC)	216	1		7			7
Conventionals							
total suspended solids (TSS)	216	1		18			18
pH (standard units)	216	1		7.6			

(a) This sample was not analyzed for toxic organic pollutants.

(b) Source water for this plant was not sampled.

TABLE V-4

PRIMARY COPPER SAMPLING DATA
SLAG GRANULATION, CONTACT, AND NON-CONTACT COOLING WATER
RAW WASTEWATER

Pollutants	Stream Code	Sample Type	Source(b)	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
23. chloroform	87	3	ND	0.022	0.104	0.015	0.047
66. bis(2-ethylhexyl) phthalate	87	3	0.036	0.100	*	0.015	0.038
115. arsenic	87	3	0.010	0.040	0.040	0.030	0.037
	215	2		0.400			0.400
118. cadmium	87	3	< 0.002	0.010	0.060	< 0.002	0.023
	215	2		< 0.005			< 0.005
119. chromium	87	3	< 0.005	0.008	0.040	0.040	0.029
	215	2		0.050			0.050
120. copper	87	3	0.020	0.400	1.000	0.300	0.567
	215	2		0.150			0.150
121. cyanide	87	3		0.001	< 0.001	< 0.001	0.0003
	215	2		0.02			0.02
122. lead	87	3	0.020	0.300	0.200	0.030	0.18
	215	2		0.120			0.120
123. mercury	87	3	0.0001	< 0.00005	< 0.00005	< 0.0001	< 0.00007
	215	2		< 0.001			< 0.001
124. nickel	87	3	< 0.005	< 0.005	0.020	< 0.005	0.007
	215	2		< 0.020			< 0.020
125. selenium	87	3	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
	215	2		0.020			0.020

TABLE V-4 (Continued)

PRIMARY COPPER SAMPLING DATA
SLAG GRANULATION, CONTACT, AND NON-CONTACT COOLING WATER
RAW WASTEWATER

Pollutants	Stream Code	Sample Type	Source(b)	Concentrations (mg/l, Except as Noted)			
				Day 1	Day 2	Day 3	Average
126. silver	87	3	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
	215	2		0.020			0.020
128. zinc	87	3	< 0.060	0.300	0.700	0.100	0.368
	215	2		0.360			0.360
Nonconventionals							
chemical oxygen demand (COD)	87	3	5	6	< 5	< 5	2
	215	2		< 2			< 2
total organic carbon (TOC)	87	3	3	1	4	6	4
	215	2		< 4			< 4
phenols (total; by 4-AAP method)	87	2		0.008	0.009	0.011	0.009
	215	2		0.042			0.042
Conventionals							
oil and grease	87	1		6	9	4	6
total suspended solids (TSS)	87	3	1	3	2	2	2
	215	2		4			4
pH (standard units)	87	1		10.6	11.3	9.3	
	215	1		7.4			

(a) No samples were analyzed for the acid extractable toxic pollutants. Three samples were analyzed for the pesticide fraction; none was reported present above its analytical quantification limit.

(b) Source water for Plant C was not sampled.

TABLE V-5

PRIMARY COPPER SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
1. acenaphthene	55	1	ND	ND	*	ND	*
	90	2	ND	0.016	ND	ND	0.016
4. benzene	55	3	ND	*	*	ND	*
6. carbon tetrachloride	90	2	ND	ND	0.02	ND	0.02
11. 1,1,1-trichlorethane	55	1	ND	ND	*	*	*
15. 1,1,2,2-tetrachloro-ethane	55	1	ND	ND	*	*	*
23. chloroform	55	1	0.057	*	*	0.057	0.019
	90	2	ND	ND	0.012	*	0.006
25. 1,2-dichlorobenzene	55	1	ND	ND	ND	ND	
	90	2	ND	ND	0.076	0.046	0.061
29. 1-1-dichloroethylene	55	1	ND	*	*	ND	*
	90	2	ND	0.034	ND	ND	0.034
30. 1-2,trans-dichloro-ethylene	55	1	ND	*	*	*	*
39. fluoranthene	55	3	ND	ND	*	ND	*
	90	2	ND	*	*	0.017	0.006
55. naphthalene	55	3	ND	ND	*	ND	*
	90	2	ND	ND	ND	ND	
66. bis(2-ethylhexyl) phthalate	55	3	7.16	2.21	1.20	0.096	1.17
	90	2	0.036	0.032	0.041	0.024	0.032
67. butyl benzyl phthalate	55	3	*	*	ND	0.051	0.026
	90	2	ND	*	0.011	*	0.004
68. di-n-butyl phthalate	55	3	*	*	0.075	*	0.025
	90	2	*	*	0.012	*	0.004
69. di-n-octyl phthalate	55	3	*	ND	0.191	*	0.096
	90	2	ND	*	0.023	ND	0.011

TABLE V-5 (Continued)

PRIMARY COPPER SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
71. dimethyl phthalate	55	3	ND	ND	*	ND	*
	90	2	ND	ND	ND	ND	
73. benzo (a) pyrene	55	3	*	ND	*	ND	*
	90	2	ND	ND	ND	ND	
75. benzo (k)fluoranthene	55	3	ND	ND	*	ND	*
	90	2	ND	ND	ND	ND	
76. chrysene	55	3	*	ND	*	*	*
	90						
78. anthracene (a)	55	3	ND	< 0.014	< 0.017	< 0.011	< 0.014
	90	2	ND	ND	0.011	*	0.006
80. fluorene	55	3	ND	ND	ND	ND	
	90	2	ND	0.221	ND	0.166	0.194
81. phenanthrene (a)	55	3					
	90						
84. pyrene	55	3	ND	ND	ND	*	*
	90	2	ND	ND	ND	ND	
85. tetrachloroethylene	55	3	*	*	ND	ND	*
	90	2	*	ND	0.021	*	0.011
87. trichloroethylene	55	3	ND	*	ND	ND	*
	90	2	ND	ND	ND	ND	
90. dieldrin				ND	**	**	**
91. chlordane	55	3	**	**	**	**	**
	90	2	ND	ND	**	**	**
92. 4,4'-DDT	55	3	ND	**	**	**	**
	90	2	ND	**	**	**	
93. 4,4'-DDE	55	3	ND	**	**	**	**
	90	2	ND	ND	ND	ND	**
95. alpha-endosulfan	55	3	ND	ND	**	**	**

TABLE V-5 (Continued)

PRIMARY COPPER SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
96. beta-endosulfan	55	3	ND	ND	**	ND	**
97. endosulfan sulfate	55	3	ND	ND	**	**	**
98. endrin	55	3	ND	ND	**	ND	**
	90	2		ND	ND	**	**
99. endrin aldehyde	55	3	**	**	ND	**	**
	90	2					
100. heptachlor	55	3	**	**	ND	**	**
	90	2	ND	**	**	**	**
101. heptachlor epoxide	55	3	**	**	**	**	**
	90	2	ND	**	ND	**	**
102. alpha-BHC	55	3	**	ND	ND	**	**
103. beta-BHC	55	3	**	**	ND	**	**
	90	2	ND	**	**	**	**
104. gama-BHC	55	3	ND	**	ND	**	**
106. PCB-1242 (b)							
107. PCB-1254 (b)	55	3	**	**	**	**	**
	90	2		**	**	**	**
108. PCB-1221 (b)							
110. PCB-1248 (c)	55	3	**	**	**	**	**
	90	2		**	**	**	**
111. PCB-1260 (c)							
112. PCB-1016 (c)							
114. antimony	55	3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	90	2	< 0.1	< 0.1	0.6	< 0.1	< 0.2
115. arsenic	55	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	90	2	0.01	0.03	0.03	0.02	0.03
117. beryllium	55	3	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	90	2	< 0.001	0.005	< 0.001	< 0.001	0.002

TABLE V-5 (Continued)

PRIMARY COPPER SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
118. cadmium	55	3	< 0.002	< 0.02	< 0.002	< 0.002	< 0.002
	90	2	< 0.002	< 0.002	0.02	0.01	0.010
119. chromium	55	3	< 0.005	0.02	0.01	0.01	0.013
	90	2	< 0.005	< 0.005	0.02	0.02	0.013
120. copper	55	3	0.06	0.02	0.01	0.02	0.017
	90	2	0.02	5	9	8	7
121. cyanide	55	3		0.002	0.003	0.002	0.002
	90	2		0.002	< 0.001	< 0.001	0.001
122. lead	55	3	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
	90	2	0.02	8	2	6	5
123. mercury	55	3	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
	90	2	0.0001	0.0001	0.0001	0.0001	0.0001
124. nickel	55	3	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	90	2	< 0.005	< 0.005	< 0.0005	< 0.0005	< 0.005
125. selenium	55	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
126. silver	55	3	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
127. thallium	55	3	< 0.1	< 0.1	< 0.1	0.2	0.07
	90	2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
128. zinc	55	3	0.060	< 0.060	< 0.060	< 0.060	< 0.060
	90	2	< 0.060	2	2	2	2
Nonconventionals							
chemical oxygen demand (COD)	55	3		14	8	12	11.33
	90	2	< 5	53	50	43	48.67
total organic carbon (TOC)	55	3		1	5	7	4.333
	90	2	3	9	9	7	8.33
phenols (total; by 4-AAP method)	55	3		0.016	0.009	0.013	0.013
	90	2		0.013	0.011	0.011	0.012

TABLE V-5 (Continued)

PRIMARY COPPER SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Conventionals							
oil and grease	55	1		9	8	2	6
	90	2		11	12	3	8.7
total suspended solids (TSS)	55	3		7	5	6	6
	90	2	1	302	7	57	122
pH (standard units)	55	1		10.2	10.2		
	90	1		10.6	11.3	9.3	

NOTE: ONLY STREAM CODE 90 APPLIES
TO PRIMARY COPPER SMELTING

(a), (b), and (c) reported together

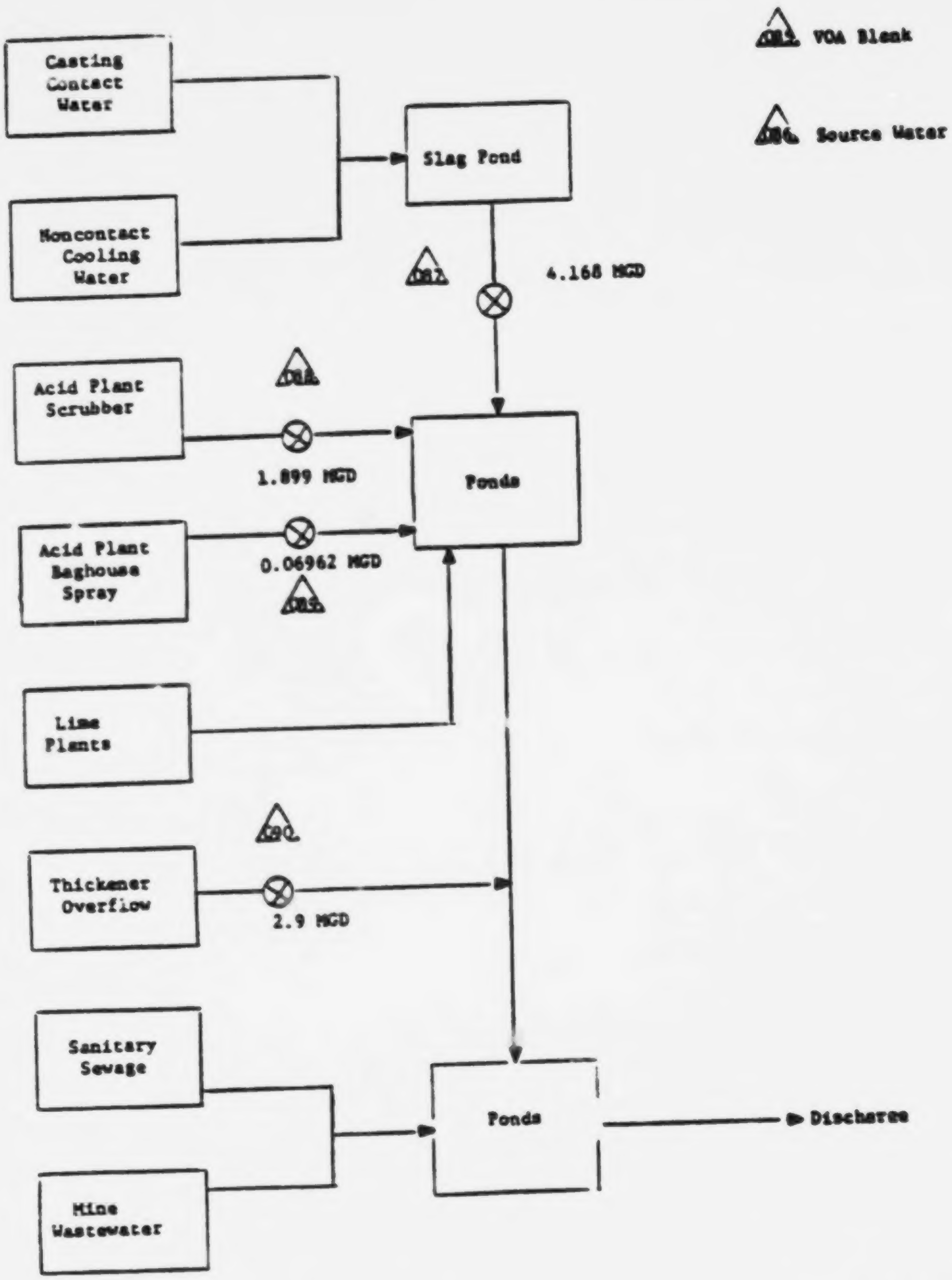
VOA Blank
082
086
Source Water
Casting Contact Water
Noncontact Cooling Water
Slag Pond
4.168 MGD
Acid Plant Scrubber
1.899 MGD
Ponds
Acid Plant Baghouse Spray
0.06962 MGD
Lime Plants
Thickener Overflow
2.9 MGD
Sanitary Sewage
Mine Wastewater
Ponds
Discharge

FIGURE V-1
SAMPLING SITES AT PRIMARY COPPER SMELTER PLANT B

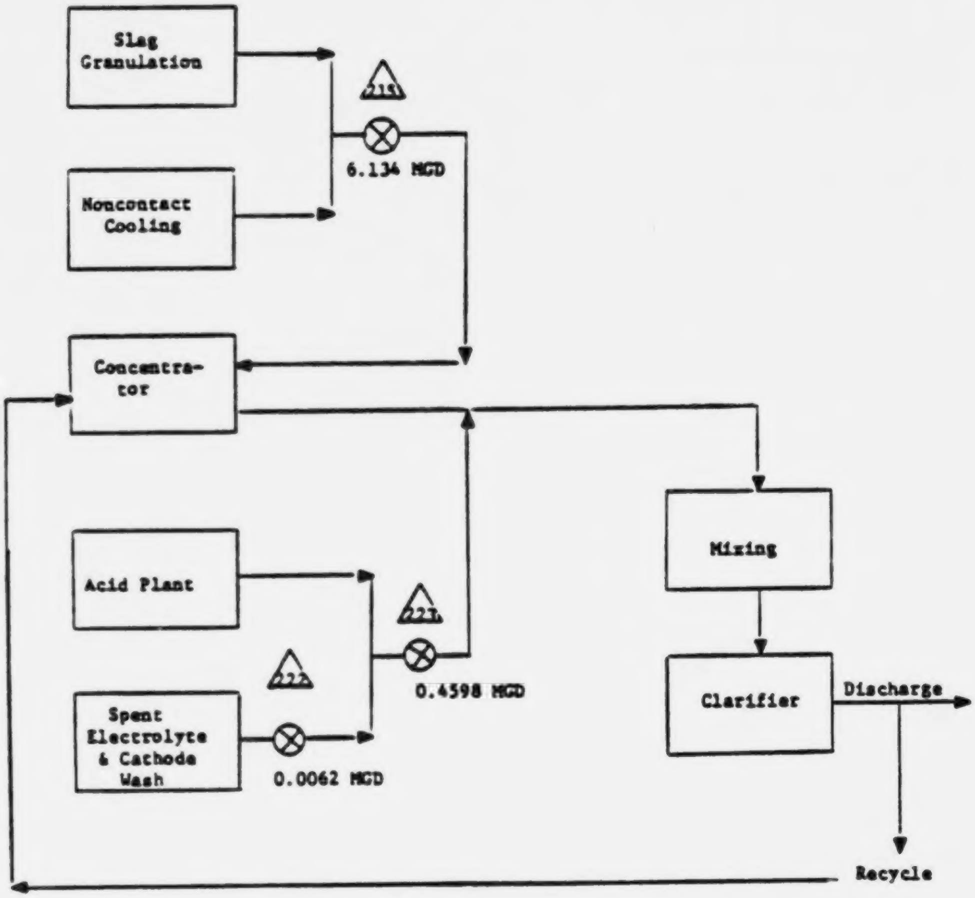
Slag Granulation
Noncontact Cooling
215
6.134 MGD
Concentrator
Acid Plant
221
0.4598 MGD
222
Spent Electrolyte & Cathode Wash
0.0062 MGD
Mixing
Clarifier
Discharge
Recycle

FIGURE V-2
SAMPLING SITES AT PRIMARY COPPER SMELTING AND REFINING PLANT C

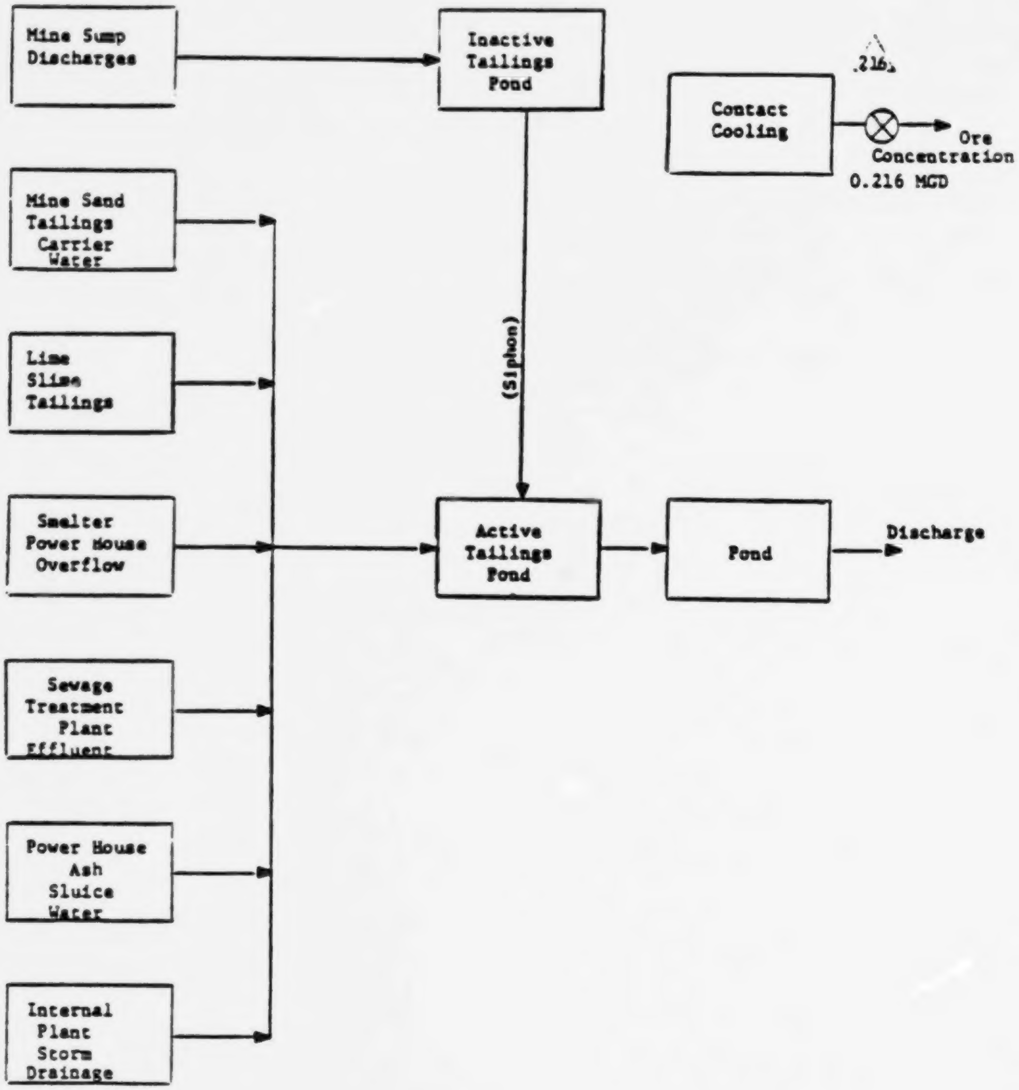
Mine Sump Discharges
Inactive Tailings Pond
.216
Contact Cooling
Ore Concentration
0.216 MGD
Mine Sand Tailings Carrier Water
Lime Slime Tailings
(Siphon)
Smelter Power House Overflow
Active Tailings Pond
Pond
Discharge
Sewage Treatment Plant Effluent
Power House Ash Sluice Water
Internal Plant Storm Drainage

FIGURE V-3
SAMPLING SITE AT PRIMARY COPPER SMELTER PLANT D

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

This section examines chemical analysis data and discusses the selection or exclusion of pollutants for potential limitation in the primary copper smelting subcategory. There were no specific pollutants selected for limitation in the primary copper smelting subcategory because there was no discharge allowance provided for this subcategory. Therefore there are no specific pollutants to review or discuss.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

The preceding sections of this supplement discussed the waste water sources, flows, and characteristics of the wastewaters from primary copper smelting plants. This section summarizes the description of these wastewaters and indicates the level of treatment which is currently practiced by the primary copper smelting industry for each waste stream.

Since the 1980 BPT regulation and the 1984 BAT, NSPS, and PSNS promulgated for primary copper smelters require no discharge of process wastewater pollutants, a discussion of the nature of process water from smelting operations is not pertinent.

SECTION VIII

COSTS, ENERGY AND NONWATER QUALITY ASPECTS

The preceding sections of this supplement discussed the waste water sources, flows, and characteristics of the wastewaters from primary copper smelting plants. This section summarizes the description of these wastewaters and indicates the level of treatment which is currently practiced by the primary copper smelting industry for each waste stream.

Since the 1980 BPT limitations required plants to achieve no discharge of process wastewater pollutants and all existing plants should have achieved that level of control, there should be no additional cost for these plants to comply with BAT because BAT is based on the same requirement.

The nature of the processes in this subcategory is such that they can be brought to no discharge by recirculation and reuse of water. These considerations do not have any adverse impact on any facet of the environment. Therefore there are no nonwater quality impacts of the regulation.

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SECTION IX

BEST PRACTICABLE TECHNOLOGY CURRENTLY AVAILABLE

EPA promulgated BPT effluent limitations for the primary copper smelting subcategory on July 2, 1980, as Subpart D of 40 CFR Part 421. EPA is not modifying these limitations. The provisions of Subpart D apply to the primary copper smelting subcategory. Under these limitations, existing point sources may not discharge process wastewater pollutants to U.S. waters except as the result of exceeding a 10-year, 24-hour rainfall event. A process wastewater impoundment which is designed, constructed and operated so as to contain the precipitation from the 10-year, 24-hour rainfall event as established by the National Climatic Center, National Oceanic and Atmospheric Administration, for the area in which such impoundment is located may discharge that volume of process wastewater which is equivalent to the volume of precipitation that falls within the impoundment in excess of that attributable to the 10-year, 24-hour rainfall event, when such event occurs.

EFFLUENT LIMITATIONS

The promulgated BPT limitations for the primary copper smelting subcategory are:

(a) Except as provided in paragraph (b) there shall be no discharge of process wastewater pollutants to navigable waters.

(b) A process wastewater impoundment which is designed, constructed and operated so as to contain the precipitation from the 10-year, 24-hour rainfall event as established by the National Climatic Center, National Oceanic and Atmospheric Administration for the area in which such impoundment is located may discharge that volume of process wastewater which is equivalent to the volume of precipitation that falls within the impoundment in excess of that attributable to the 10-year, 24-hour rainfall event, when such event occurs.

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

These effluent limitations are based on the best control and treatment technology used by a specific point source within the industrial category or subcategory, or by another category where it is readily transferable. Emphasis is placed on additional treatment techniques applied at the end of the treatment systems currently used for BPT, as well as reduction of the amount of water used and discharged, process control, and treatment technology optimization.

The factors considered in assessing best available technology economically achievable (BAT) include the ages of equipment and facilities involved, the process used, process changes, nonwater quality environmental impacts (including energy requirements), and the costs of application of such technology (Section 304 (b) (2) (B) of the Clean Water Act). At a minimum, BAT represents the best available technology economically achievable at plants of various ages, sizes, processes, or other characteristics. Where the Agency has found the existing performance to be uniformly inadequate, BAT may be transferred from a different subcategory or category. BAT may include feasible process changes or internal controls, even when not in common industry practice.

The required assessment of BAT considers costs, but does not require a balancing of costs against effluent reduction benefits (see Weyerhaeuser v. Costle, 590 F.2d. 1011 (D.C. Cir. 1978)). However, in assessing BAT, the Agency has given substantial weight to the economic achievability of the technology.

TECHNICAL APPROACH TO BAT

The Agency reviewed a wide range of technology options and evaluated the available possibilities to ensure that the most effective and beneficial technologies were used as the basis of BAT. Since no discharge of process wastewater pollutants from the primary copper smelting subcategory is the basis of promulgated BAT limitations, (except during a 25-year, 24-hour storm) it was not necessary to examine treatment options for this subcategory.

STORM WATER AND PRECIPITATION ALLOWANCES

The interim BAT effluent limitations promulgated on February 27, 1975 included net precipitation and catastrophic storm allowances. Primary copper smelters were allowed a discharge of process wastewater which is equivalent to the volume of precipitation that falls within the wastewater impoundment in excess of that attributable to the 25-year, 24-hour rainfall event, when such event occurs. In addition, smelters were allowed to discharge a volume of process wastewater on a monthly basis that is equal to the net difference between the rainfall falling on the impoundment and the mean evaporation from the pond water surface. This monthly discharge was subject to concentration-based standards, whereas the catastrophic storm was not subject to any effluent limitations.

EPA modified the primary copper smelting and electrolytic refining precipitation allowances for BPT in the 1980 rulemaking However, no modifications were made to BAT in that rule. The Agency is modifying its approach to excess precipitation for BAT to be consistent with the excess precipitation limitations in the amended BPT. Wastewater generated at primary copper smelters is due primarily to slag granulation and anode casting contact cooling, which can be recycled or reused in other plant processes. There is no monthly allowance for net precipitation from cooling impoundments because they require much smaller surface areas than evaporative impoundments. The Agency is, however, retaining the catastrophic storm water allowances for the 25-year, 24-hour storm event for the primary copper smelting subcategory.

EFFLUENT LIMITATIONS

The promulgated BAT for the primary copper smelting subcategory is zero discharge, subject to a discharge allowance for storm water resulting from a 25-year, 24-hour storm. When such a storm occurs, primary copper smelters are allowed to discharge a volume of process water in excess to that attributable to the 25-year, 24-hour storm that falls on the wastewater cooling impoundment. The effluent quality of this discharge is not controlled.

The promulgated BAT limitations for the primary copper smelting subcategory are:

(a) Subject to the provisions of paragraph (b), there shall be no discharge of process wastewater pollutants into navigable waters.

(b) A process wastewater impoundment which is designed, constructed and operated so as to contain the precipitation from the 25-year, 24-hour rainfall event as established by the National Climatic Center, National Oceanic and Atmospheric Administration for the area in which such impoundment is located may discharge that volume of process wastewater which is equivalent to the volume of precipitation that falls within the impoundment in excess of that attributable to the 25-year, 24-hour rainfall event, when such event occurs.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology (BDT). New plants have the opportunity to design the best and most efficient production processes and wastewater treatment technologies without facing the added costs and restrictions encountered in retrofitting an existing plant. Therefore, Congress directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible. This section describes technologies for treatment of wastewater from new sources, and presents mass discharge standards of regulated pollutants for NSPS based on the selected treatment technology.

TECHNICAL APPROACH TO BDT

All of the treatment technology options applicable to a new source were previously considered for BAT. Because no discharge of process wastewater pollutants is the most rigorous requirement and that requirement is imposed by the existing BPT limitation, there are no more stringent requirements which can be made at this level of regulation.

STORM WATER AND PRECIPITATION ALLOWANCES

Storm water allowances are eliminated under NSPS for the primary copper smelting subcategory. New plants can be constructed with demonstrated cooling tower technology rather than cooling impoundments to cool and recirculate casting contact cooling water and slag granulation wastewater. The retrofit cost of adding cooling towers to replace cooling impoundments may be cost prohibitive for existing sources. However, new sources will not have this constraint on their operations.

NEW SOURCE PERFORMANCE STANDARDS

The standard of performance for new sources is:

There shall be no discharge of process wastewater pollutants into navigable waters.

SECTION XII

PRETREATMENT STANDARDS

Section 307(b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES), which must be achieved within three years of promulgation. PSES are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of publicly owned treatment works (POTW). The Clean Water Act of 1977 requires pretreatment for pollutants, such as heavy metals, that limit POTW sludge management alternatives. Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect discharge facilities, like new direct discharge facilities, have the opportunity to incorporate the best available demonstrated technologies, including process changes, in-plant controls, and end-of-pipe treatment technologies, and to use plant site selection to ensure adequate treatment system installation. Pretreatment standards are to be technology-based, analogous to the best available technology for removal of toxic pollutants.

There are no indirect discharging primary copper smelting plants in the United States. Consequently, the Agency is not promulgating pretreatment standards for existing sources.

TECHNICAL APPROACH TO PSNS

All of the treatment technology options applicable as pretreatment were previously considered for BAT. Because no discharge of process wastewater pollutants is the most rigorous requirement and that requirement is imposed by the existing BPT limitation, there are no more stringent requirements which can be made at this level of regulation.

STORM WATER AND PRECIPITATION ALLOWANCES

Precipitation allowances are eliminated under PSNS for the primary copper smelting subcategory. New plants can be constructed with demonstrated cooling tower technology rather than cooling impoundments to cool and recirculate casting contact cooling water and slag granulation wastewater. The retrofit cost of adding cooling towers to replace cooling impoundments may be cost prohibitive for existing sources. However, new sources will not have this constraint on their operations.

PRETREATMENT STANDARDS FOR NEW SOURCES

The pretreatment standard for new sources is: There shall be no discharge of process wastewater pollutants into navigable waters.

SECTION XIII

BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY

EPA is not promulgating best conventional pollutant control technology (BCT) for the primary copper smelting subcategory at this time.

NONFERROUS METALS MANUFACTURING POINT SOURCE CATEGORY

DEVELOPMENT DOCUMENT SUPPLEMENT

for the

Primary Electrolytic Copper Refining Subcategory

William K. Reilly
Administrator

Rebecca Hanmer
Acting Assistant Administrator for Water

Martha Prothro, Director
Office of Water Regulations and Standards

Thomas P. O'Farrell, Director
Industrial Technology Division

Ernst P. Hall, P.E., Chief
Metals Industry Branch
and
Technical Project Officer

May 1989

U.S. Environmental Protection Agency
Office of Water
Office of Water Regulations and Standards
Industrial Technology Division
Washington, D. C. 20460

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1082-1088

PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

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PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

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SECTION I

SUMMARY

On February 27, 1975 (40 FR 8514), EPA promulgated interim technology-based effluent limitations for existing sources and proposed new source performance and pretreatment standards for the primary copper subcategory of the nonferrous metals manufacturing point source category. These effluent guidelines and standards limited the quantities of total suspended solids, copper, cadmium, lead, zinc, and pH in primary copper subcategory wastewaters.

For primary electrolytic copper refiners not located on-site with primary copper smelters, the interim BPT regulation allowed the discharge of process wastewater from electrolytic refining and casting subject to mass limitations for facilities located in areas of net precipitation.

The 1975 BPT limitations for copper refining required zero discharge of all process wastewater for facilities located in net evaporation areas with two rainfall related exceptions. When a 10-year 24-hour rainfall event occurred, refiners were allowed to discharge a volume of water equal to that resulting from the 10-year 24-hour rainfall event falling within a refiners wastewater impoundment. In addition, a discharge of process wastewater was permitted during a calendar month equal to the difference between the net evaporation and precipitation for that month. This monthly rainfall allowance was subject to concentration-based limitations. For those refiners located in areas of net precipitation, a discharge of process wastewater was allowed in accordance with mass-based limitations.

The 1975 BAT limitations for refineries not located on-site with smelters and in areas of net evaporation required discharge standards similar to the BAT primary copper smelting standards. For facilities located in areas of net precipitation, a constant discharge of refining wastewater was allowed subject to mass limitations.

Revised BPT limitations were issued for the primary electrolytic copper refining subcategory on July 2, 1980 (45FR44926). The major modification to the interim regulation was to delete the net precipitation provisions and allow a constant discharge of process wastewater from all refiners regardless of location and subject them to mass limitations.

In the March 1984 rulemaking (49FR8742) EPA promulgated modifications to BAT, NSPS, and PSNS for this subcategory pursuant to the provisions of Sections 301, 304, 306 and 307 of the Clean Water Act as amended. This supplement provides a compilation and analysis of the background material used to develop these effluent limitations and standards. The BPT regulations which were promulgated in 1980 remain unchanged, and are discussed later for information purposes.

The primary electrolytic copper refining subcategory is comprised of 14 plants. Of the 14 plants, three discharge directly to rivers , lakes and streams; none discharge indirectly through publicly owned treatment plants (POTW); and 11 achieve zero discharge of process wastewaters.

EPA first studied the primary electrolytic copper refining subcategory to determine whether differences in raw materials, final products, manufacturing processes, equipment, age and size of plants, and water usage required the development of separate effluent limitations and standards for different segments of the subcategory. This involved a detailed analysis of wastewater discharge and treated effluent characteristics, including (1) the sources and volume of water used, the processes employed, and the sources of pollutants and wastewaters in the plant; and (2) the constituents of wastewaters, including toxic pollutants.

EPA also identified several distinct control and treatment technologies (both in-plant and end-of-pipe) applicable to primary electrolytic copper refining. The Agency analyzed both historical and newly generated data on the performance of these technologies, including their nonwater quality environmental impacts (such as air quality impacts and solid waste generation) and energy requirements. EPA also studied various flow reduction techniques reported in the data collection portfolios (dcp) and plant visits.

Engineering costs were prepared for each of the control and treatment options considered for the subcategory. These costs were then used by the Agency to estimate the impact of implementing the various options on the subcategory. For each control and treatment option that the Agency found to be most effective and technically feasible in controlling the discharge of pollutants, the number of potential closures, number of employees affected, and impact on price were estimated. These results are reported in a separate document entitled Economic Impact Analysis of Effluent Limitations Guidelines and Standards for the Nonferrous Smelting and Refining Industry.

Based on consideration of the above factors, EPA identified various control and treatment technologies which formed the basis of BAT, and selected control and treatment appropriate for each set of standards and limitations. The limitations and standards for BPT, BAT, NSPS, and PSNS are presented in Section II.

For BAT, the Agency has built upon the primary electrolytic copper refining BPT basis by adding in-process control technologies which include recycle of process water from air pollution control and metal contact cooling wastewater streams. Filtration is added as an effluent polishing step to the end-of-pipe treatment. For one plant, sulfide precipitation and pressure filtration is added before lime precipitation and sedimentation to assure achieving the performance of lime, settle, and filter technology. To meet the BAT effluent limitations based on this technology, the primary electrolytic copper refining subcategory is estimated to incur a capital cost of $0.266 million (1982 dollars) and an annual cost of $0.171 million (1982 dollars).

The best demonstrated technology (BDT), which is the technical basis of NSPS, is equivalent to BAT. In selecting NSPS, EPA recognized that new plants have the opportunity to implement the best and most efficient manufacturing processes and treatment technology. As such, the technology basis of BAT has been determined as the best demonstrated technology.

The Agency is not promulgating pretreatment standards for existing source (PSES) since there are no indirect discharging plants in the primary electrolytic copper refining subcategory. The technology basis for pretreatment standards for new sources (PSNS) is the best demonstrated. As such, the PSNS are identical to NSPS for all waste streams.

SECTION II

CONCLUSIONS

EPA has divided primary copper plants into two subcategories: the primary copper smelting subcategory and the primary electrolytic copper refining subcategory. The primary electrolytic copper refining subcategory has been divided into five subdivisions for the purpose of effluent limitations and standards. These subdivisions are:

(a) Anode and cathode rinse,
(b) Spent electrolyte,
(c) Casting contact cooling,
(d) Casting wet air pollution control, and
(e) By-product recovery.

EPA promulgated BPT effluent limitations for the primary electrolytic copper refining subcategory on July 2, 1980 (45FR44926) as Subpart E of 40 CFR Part 421. No modifications are now being promulgated for the 1980 BPT.

BPT effluent limitations for the primary electrolytic copper refining subcategory were promulgated based on the performance achievable by the application of chemical precipitation and sedimentation (lime and settle) technology. The following BPT effluent limitations were promulgated for existing sources:

	Effluent Limitations	
Pollutant or Pollutant Property	Maximum for Any One Day	Average of Daily Values for 30 Consecutive Days Shall not exceed
	Metric units, kg/kkg of product; English units, lbs/1,000 lb of product	
Total Suspended Solids	0.100	0.050
Copper	0.0017	0.0008
Cadmium	0.0006	0.00003
Lead	0.0006	0.00026
Zinc	0.0012	0.0003
pH	Within the range of 6.0 to 9.0	

EPA has amended BAT effluent limitations based on the performance achievable by the application of in-process flow reduction and end-of-pipe treatment technology consisting of chemical precipitation, sedimentation, and multimedia filtration (lime, settle, and filter) technology. The following BAT effluent limitations are promulgated for existing sources:

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(a) Casting Contact Cooling

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of copper cast English Units - lbs/million lbs of copper cast	
Arsenic	0.692	0.309
Copper	0.638	0.304
Nickel	0.274	0.184

(b) Anode and Cathode Rinse

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of cathode copper production English Units - lbs/million lbs of cathode copper production	
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000

(c) Spent Electrolyte

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of cathode copper production English Units - lbs/millions lbs of cathode copper production	
Arsenic	0.068	0.031
Copper	0.063	0.030
Nickel	0.027	0.018

(d) Casting Wet Air Pollution Control

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of casting production English Units - lbs/million lbs of casting production	
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000

(e) By-Product Recovery

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of product recovered from electrolytic slimes processing English Units - lbs/million lbs of product recovered from electrolytic slimes processing		
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000

NSPS are promulgated based on the performance achievable by the application of chemical precipitation, sedimentation, and multimedia filtration (lime, settle, and filter) technology and in-process flow reduction control methods. The following effluent standards are promulgated for new sources:

(a) Casting Contact Cooling

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of copper cast English Units - lbs/million lbs of copper cast		
Arsenic	0.692	0.309
Copper	0.638	0.304
Nickel	0.274	0.184
TSS	7.470	5.976
pH	Within the range of 7.0 to 10.0 at all times	

(b) Anode and Cathode Rinse

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of cathode copper production English Units - lbs/million lbs of cathode copper production		
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000
TSS	0.000	0.000
pH	Within the range of 7.0 to 10.0 at all times	

(c) Spent Electrolyte

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of cathode copper production English Units - lbs/million lbs of cathode copper production	
Arsenic	0.068	0.031
Copper	0.063	0.030
Nickel	0.027	0.018
TSS	0.735	0.588
pH	Within the range of 7.0 to 10.0 at all times	

(d) Casting Wet Air Pollution Control

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of copper casting production English Units - lbs/million lbs of copper casting production	
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000
TSS	0.000	0.000
pH	Within the range of 7.0 to 10.0 at all times	

(e) By-Product Recovery

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of product recovered from electrolytic slimes processing English Units - lbs/million lbs of product recovered from electrolytic slimes processing	
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000
TSS	0.000	0.000
pH	Within the range of 7.0 to 10.0 at all times	

EPA is not promulgating pretreatment standards for existing sources (PSES) in the primary electrolytic copper refining subcategory since there are no existing indirect dischargers in this subcategory.

PSNS are promulgated based on the performance achievable by the application of chemical precipitation, sedimentation, and multimedia filtration (lime, settle, and filter) technology and in-process flow reduction control methods. The following pretreatment standards are promulgated for new sources:

(a) Casting Contact Cooling

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of copper cast English Units - lbs/million lbs of copper cast		
Arsenic	0.692	0.309
Copper	0.638	0.304
Nickel	0.274	0.184

(b) Anode and Cathode Rinse

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of cathode copper production English Units - lbs/million lbs of cathode copper production		
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000

(c) Spent Electrolyte

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of cathode copper production English Units - lbs/million lbs of cathode copper production		
Arsenic	0.068	0.031
Copper	0.063	0.030
Nickel	0.027	0.018

(d) Casting Wet Air Pollution Control

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of casting production English Units - lbs/million lbs of casting production		
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000

(e) By-Product Recovery

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Metric Units - mg/kg of product recovered from electrolytic slimes processing English Units - lbs/million lbs of product recovered from electrolytic slimes processing		
Arsenic	0.000	0.000
Copper	0.000	0.000
Nickel	0.000	0.000

SECTION III

SUBCATEGORY PROFILE

This section of the primary electrolytic copper refining supplement describes the raw materials and processes used in electrolytically refining copper bearing raw materials to produce pure (99.99%) copper and presents a profile of the primary electrolytic copper plants identified in this study.

DESCRIPTION OF PRIMARY COPPER PRODUCTION

The manufacturing of copper from copper sulfides through pyrometallurgical processes usually produces a raw metal product which must be further refined before use. Hydrometallurgical processes are also used to process copper concentrates and this is the chief process used to process copper oxide, but it also may be used to process copper sulfides. The products from both pyrometallurgical and hydrometallurgical processes require further refining. The commonly used steps in electrolytic refining are tabulated below.

Primary Electrolytic Refining

1. Electrolytic refining
2. Electrowinning
3. Casting
4. By-product recovery

In addition to the smelting and refining of copper, several facilities also recover precious metals from insoluble wastes (anode slimes) generated during electrolytic refining. Precious metals present within the slimes may include silver, selenium, tellurium, gold, platinum, and palladium. Recovery of these metals from refinery wastes will be discussed with emphasis on sources of wastewater within each recovery process.

RAW MATERIALS

There are approximately 160 known copper minerals, about a dozen of which are commercially important. The most important copper ores in the United States are chalcopyrite, chalcocite, covellite, chrysocolla, bornite, cuprite, and malachite. These are either sulfide, silicate, or oxide ores. Most of the copper ore processed in the United States is a copper sulfide. At the mine site, copper bearing ore is concentrated into copper sulfide which forms the main raw material for copper smelting.

Roasting, smelting, converting, fire refining and casting of the blister copper from copper bearing ores is discussed in the Primary Copper Smelting Subcategory Supplement.

ELECTROLYTIC REFINING

More extensive refining of copper is usually necessary if it is to be used in electrical applications. By using electrolysis, the copper can be refined to a purity of 99.98 percent or greater, and the precious metals contained as impurities in the copper can be recovered. Fire refined or blister copper from the smelting operation, sulfuric acid, and copper sulfate are the principal raw materials used in electrolytic refining. For use in a refinery, blister copper is cast into anodes which are rectangular plates with lugs or hooks on two corners used for hanging. Each anode weighs approximately 460 pounds.

At the refinery, anodes and starter sheets of refined copper are suspended in solutions of sulfuric acid and copper sulfate. Through electrolysis, positive copper ions from the anode migrate through the copper sulfate-sulfuric acid medium and are deposited on the starter sheet which has become the cathode. To drive the reaction, an electric current is passed through each cell. The migration of the copper ion takes place through the following anode-cathode reaction:

Anode: $Cu \text{ ----> } Cu^{2+} + 2e$

Cathode: $Cu^{2+} \text{ ----> } 2e + Cu$

Impurities released into the electrolyte either go into solution or settle to the bottom of the tank. The electrolyte is continuously circulated through the system of cells with a small slip stream removed for purification to control the amount of dissolved solids. Those impurities settling to the bottom of each tank are commonly referred to as anode slimes and are removed from the bottom of each cell. Further processing of the slimes may be done on site to recover the precious metals contained within the slime as a by-product of copper refining or they may be sold to outside refiners.

After approximately two weeks, when the cathodes reach a designated size, generally 180 pounds, they are removed and rinsed. Another set of starter sheets is inserted with the anodes for another two week period. At the end of the second cycle, both the cathodes and anodes are removed. The anodes are not completely consumed, but if they were left in the cell they soon would break, falling into the cell and short-circuiting it. Scrap anodes may be rinsed and then returned back to anode casting. The cathodes are either sold and shipped with no further refining, or they are cast into wire bar, ingots, or billets for copper forming operations. A block diagram illustrating the electrolytic refining process is shown in Figure III-1 (page 1121).

In a cell, the number of anodes and cathodes is dependent on the size of the cell and the spacing between anodes and cathodes. Normally an electrolytic cell contains 30 to 40 anodes and cathodes. In a tank house, the number of cells is usually between 1,000 and 2,000. Circulation of the electrolyte is done to prevent separation of the sulfuric acid and copper sulfate.

The electrolyte is removed from the top of each cell and introduced into the bottom of the next cell. The electric current passing through each cell moves from anode to cathode in the cell, and is then transmitted to the next cell through the support bars.

ELECTROWINNING

As mentioned earlier, a slip stream of electrolyte is removed from the tank house for purification. Removal of soluble impurities and excess copper in the electrolyte must be controlled to maintain an optimum refining process. Significant soluble impurities are nickel and arsenic; however, the major impurity in the anode copper is copper oxide, Cu_2O. When copper oxide is released into the electrolytic solution, it reacts with the sulfuric acid forming copper sulfate:

$$Cu_2O + H_2SO_4 \text{ ----> } CuSO14 + Cu + H_2O$$

As the copper sulfate concentration approaches saturation, it will begin to precipitate and settle to the bottom of the tank. The copper molecule released into the solution when copper oxide reacts with the sulfuric acid settles to the bottom of the tank because it is not electrically charged. Impurities settling to the bottom of each tank are removed for further processing to recover precious metals.

Processing the spent electrolyte is accomplished with various methods, but the most popular uses a two-stage process. In the first step, commonly referred to as electrowinning, copper is removed from solution by electrolysis in much the same way as was done in the tank house. The major difference is that an insoluble anode, such as lead or iron, is used. Copper is forced out of the solution and plated onto a cathode. This process uses two to three liberator cells connected in a series. In the first cell, the cathode copper is of high purity with slight lead contamination and may be used with no additional refining. As the copper concentration in the electrolyte decreases, the purity of the copper cathode also decreases. Recovered copper from the last two liberator cells is returned for smelting or anode casting, depending on the purity.

The last liberator cell must be hooded to control arsine gas, AsH_3. As the copper is depleted from the spent electrolyte, arsenic begins to react with hydrogen. Hoods above the cell collect this poisonous gas and disperse it safely to the atmosphere. The arsenic that does not escape as arsine gas is collected as a sludge and returned to the smelter.

The spent electrolyte is now composed of nickel sulfate and sulfuric acid. Through evaporation, the decopperized solution is concentrated and then cooled. As the solution cools, nickel sulfate is precipitated, leaving what is known as black acid. The acid is usually recycled back to the refining process, but it may be used for leaching operations or fertilizer manufacture.

Wastewater generated from copper refining is due to cathode and anode rinse water and the discharge of spent electrolyte. Normally the anodes and cathodes are rinsed above the electrolytic cells so that the rinse water is captured in the electrolytic cells. Discharge of spent electrolyte is not generally practiced since the electrolyte can be recycled to the refining process after electrowinning. One hundred percent reuse of the spent acid after treatment is site-specific. The magnitude of impurities in the electrolyte is a function of the raw material. Those plants containing low nickel values have difficulty recycling spent acid. If the nickel concentration is allowed to increase so that nickel sulfate can be recovered, other impurities increase in the electrolyte which affect product quality. Currently one of the 14 copper refiners discharges spent electrolyte. Although a wet scrubber could be used to control arsine gas, no plant reported use of wet scrubbers for this purpose.

CASTING

Casting is the final step for copper refining. Electrolytic copper is cast into wire bar or billets for eventual use in the forming processes. Wastewater associated with casting is due primarily to furnace scrubber liquor and casting contact cooling water. One plant currently is using a wet scrubber to control air pollution emissions from its casting furnaces. There are nine plants that discharge casting contact cooling water.

BY-PRODUCT RECOVERY

Many of the impurities found within blister copper have economic value and may be recovered as a by-product of the electrolytic copper refining process. During electrolysis, impurities present in the anode are released into solution. The soluble impurities include arsenic and nickel, while those that are not soluble, and settle to the bottom of the tank, include silver, selenium, tellurium, gold, platinum, and palladium. For a facility to recycle its spent electrolyte after electrowinning, the concentration of the nickel sulfate must be reduced to insure optimum operating conditions in the tank house.

Six plants reported in their dcp recycling 99 percent or more of their electrolyte. At the same time, there were six plants that reported processing slimes on site to recover precious metals. Three plants currently operate by-product recovery processes. In the discussions that follow, a brief description of the methods used to recover these metals and the wastewater generated from their recovery will be presented.

Nickel Sulfate Recovery

The bleed stream removed from the copper electrolytic tank house is composed primarily of sulfuric acid, copper sulfate, and nickel sulfate. Removal of copper sulfate from the electrolyte, as discussed earlier, is similar to the copper refining process in that electrolysis is used. The major difference, however, is an insoluble anode replaces the copper anodes used in the tank house. The decopperized solution still contains nickel sulfate, among others, as an impurity. Removal of the soluble nickel is accomplished through partial evaporation to initiate the precipitation of nickel sulfate. The spent electrolyte can then be recirculated back to the tank house or sold for use in the manufacture of fertilizer. The nickel sulfate may be marketed with no further refining, or a vacuum crystallizer may be used to produce a more refined product.

Noncontact wastewater generated from the recovery of nickel sulfate occurs if a barometric condenser is used when additional refining takes place.

Silver Recovery

As mentioned earlier, anode slimes removed from the bottom of the electrolytic cells contain varying amounts of precious and base metals, specifically silver, selenium, tellurium, gold, platinum, palladium, and copper. The principal component of the slimes is copper, which may account for as much as 30 percent of the slime. Preliminary treatment of the slime to remove copper is essential to enhance the silver recovery process. To begin, the slime is passed through a trammel screen to remove copper sulfate precipitate. The slime is fed into a revolving cylindrical screen (trammel) at one end, the copper sulfate drops through the holes, and the slime is delivered at the other end. The remaining copper is leached from the slime using a variety of methods such as sulfuric acid, hexavalent chromium, or solubilizing the copper and leaching with water. The leachate is then returned to the electrowinning process to recover the copper. The remaining slime is filtered and pressed to form a cake for further processing in a cupel furnace. A cupel furnace is a small scale reverberatory furnace that is refractory lined with heat supplied between the roof and charge.

As shown in Figure III-2 (page 1122), pressed, filtered slimes and fluxes (iron, silica, and limestone) are charged to a cupel furnace. Impurities react with the fluxing agents, forming slag, and are removed from the top of the furnace. Dore, the remaining metallic material, is approximately 95 percent silver, while the soda slag consists primarily of selenium and tellurium. Also removed from the furnace is a slag containing recoverable concentrations of lead which are sent to a lead smelter.

During the silver smelting operation, selenium volatilizes and leaves the furnace with the off-gases. Consequently, wet scrubbers are used to capture the selenium and return it for further processing as described later.

One plant charges anode slimes directly to kilns after removing the copper sulfate with filters. In the kilns, the slimes are fused and selenium volatilizes. Wet scrubbers capture the selenium for further processing. This plant also uses a wet scrubber to control sulfur dioxide (SO_2) fumes in the kiln off-gases. The plant discharges the scrubber wastewater to its wastewater treatment plant but the flow is negligible when compared to other plant flows. Copper is leached from the "fused" slimes, as described above, and charged to a cupel furnace to produce dore. Wet scrubbers are used on the dore furnace to recover precious metal particulates that may be present in the off-gases. The scrubber water is recycled to the copper leaching operation.

An electrolysis process is used to recover silver in the dore metal. In this electrolytic process, dore is cast into anodes approximately 20 inches square and one inch thick. Several anodes are suspended in an electrolytic medium consisting of copper nitrate and silver nitrate. Each anode is suspended on glass rods with a filter basket suspended under the anodes. In this configuration, the bottom of the cell becomes the cathode where silver crystals form. Gold slimes released into the solution are captured in the filter basket and removed for further processing. Silver crystals forming on the bottom of the cell are removed every three to four hours, washed, and then cast into silver bricks using an induction furnace.

Wastewaters are usually not discharged from this process because each potential waste stream contains economically important quantities of silver, selenium, and tellurium. The silver nitrate used as the electrolyte medium is recycled, while the cupel furnace or fusion kiln scrubber liquors contain approximately one half the selenium present in the charge. Consequently, the scrubber liquor is used during the processing of the soda slag to extract the selenium and tellurium present in the scrubber liquor and slag. However, there are two waste streams currently discharged to treatment at one copper plant. Contact cooling water used during the casting of dore anodes is sent to a central wastewater treatment plant. Also, wastewater from the fusion kiln SO_2 scrubber is treated at the same facility.

Gold Recovery

Gold slimes captured in the silver electrolytic cells are processed in bench-scale operations through leaching with hot sulfuric acid to remove any residual silver entrained in the slime. The gold is recovered either electrolytically or using dissolution and precipitation steps. In the electrolytic method, gold is refined in a heated electrolytic cell using a silver chloride medium as shown in Figure III-3 (page 1123). Impurities present at this stage include platinum and palladium slimes, which are recovered by further processing. An induction furnace is used to melt and cast the gold which is approximately 99.9 percent pure.

The potential for wastewater in this process is due primarily to spent leachate from the preliminary silver preleaching step.

Spent leachate is treated through cementation to recover minor amounts of silver and gold. Since this is a small scale operation, the volume of leachate is negligible and will not affect the design or performance of the plant treatment system.

In the precipitation method, the solids containing gold are dissolved in aqua regia (one part concentrated nitric acid and three to four parts hydrochloric acid). Aqua regia is the only known reagent that dissolves gold. The gold is precipitated from solution with sulfur dioxide or chlorine gas. Gold precipitate is removed from solution by filtration. The filtrate, which contains palladium and platinum, is further processed. The gold solids are cast into anodes to be further refined electrolytically. The purified gold is collected on cathodes which are then melted and cast in an induction furnace. Spent electrolyte and water used to wash cathodes is reused in the electrolytic cell or treated and recycled as makeup water.

Palladium Recovery

Slimes from gold electrolytic separation and solutions from gold precipitation steps contain recoverable amounts of palladium and platinum. Palladium is usually recovered first, using either an electrolytic separation or a dissolution and precipitation method as shown in Figure III-4 (page 1124). The electrolytic method is similar to the electrolytic separations used for silver and gold. Palladium and platinum slimes from the gold electrolytic cell are melted and cast into anodes. Palladium is then collected on a cathode in another electrolytic cell and the platinum is released into solution. The palladium cathodes are melted and cast as final product. Platinum slimes are captured at the bottom of the cell and further processed. Spent electrolyte is reused in the electrolytic cell or reprocessed in the copper slimes leaching step described above.

In the precipitation method, palladium and platinum are recovered by precipitating them as palladium and platinum chloride, usually using ammonium chloride. Filtration is used to separate the precipitates from the non-precious metals solution, which is treated and reused at the one plant with this process. The filter cake is then dissolved in solution with chlorine gas or hydrochloric acid. The platinum remains as a solid and is removed for further processing. The palladium is purified using a series of dissolution and precipitation steps. Palladium is precipitated from solution with hydrochloric acid and separated by filtration. The filtered metal may be washed to remove residual acid and impurities. Ammonium hydroxide is then used to dissolve the metal and the precipitation and filtration steps are repeated. When palladium of sufficient purity is obtained, the metal is calcined, then crushed or ground into powder.

The sources of wastewater from this process are the precipitation, filtration, and washing steps. At the plant currently using this process, these solutions are treated and reused as makeup water for other processes. This plant uses a wet scrubber to control acid and base fumes from the dissolution and precipitation steps. The same scrubber controls fumes from the platinum precipitation process. The scrubber wastewater is neutralized and reused in other plant processes.

Platinum Recovery

Platinum is recovered from slimes from palladium electrolytic separation and from impure platinum precipitated in the palladium precipitation process. Figure III-5 (page 1125) schematically depicts the two methods used for platinum recovery. Platinum from slimes is usually recovered in an electrolytic cell. Slimes are melted and cast into anodes. The electrolytic process results in platinum cathodes which are melted and cast as platinum metal. Spent electrolyte and cathode wash water are possible sources of wastewater. However, this water is recycled within the cell or reprocessed in the copper slimes leaching step described above.

Impure platinum precipitated in the palladium precipitation process is purified through a series of dissolution and precipitation steps, much like palladium. First, impurities and residual palladium are dissolved with a hydrochloric and nitric acid mixture. Following filtration and washing, the filtrate is sent to the palladium recovery process. The filter cake, which contains platinum, is dissolved with hydrochloric acid. Ammonium chloride is then added to precipitate platinum chloride. The platinum chloride is filtered and washed. The filter cake is calcined, ground, and recalcined to form the final platinum product.

Wastewater generated at the one plant currently using which process consists of supernatant, filtrate, and wash water from the precipitation and filtration steps. This wastewater is treated and reused in other plant processes. This plant uses a wet scrubber to control acid and base fumes from the platinum dissolution and precipitation steps. The same scrubber is used on the palladium precipitation process. The scrubber wastewater is neutralized and reused in other plant processes.

Selenium Recovery

As discussed earlier, volatile selenium gas escaping from the cupel furnace or fusion kiln is collected with wet scrubbers. This scrubber liquor is acidified with nitric acid and mixed with ground soda-niter slag ($NaNO_3$) from the cupel furnace containing selenium and tellurium. When these two materials are mixed, tellurium precipitates as TeO_2 and is removed for further processing. The remaining solution is neutralized and then the selenium is precipitated by adding hydrochloric acid, sulfuric acid, steam, and sulfur dioxide. The selenium precipitate is filtered, dried, and marketed. Spent and dirty solution from the precipitation and filtration of selenium is treated with sulfuric acid, hydrochloric acid, and sulfur dioxide to precipitate low grade selenium which is returned to the cupel furnace. An illustration of this process is shown in Figure III-6 (page 1126).

Spent solutions are generated from the precipitation and filtration steps. Specifically, spent solution after selenium precipitation and filtration, and sludge removal from the selenium scrubber liquor are possible sources of wastewater. This waste water is recycled to recovery processes, such as copper slimes leaching, or treated and reused in other plant processes.

One plant operates a wet scrubber to capture metal particulates in the selenium drier off-gases. The scrubber wastewater is sent to the copper slimes leaching operation for metals recovery.

Tellurium Recovery

During the processing of selenium, tellurium is precipitated as TeO_2 and removed from the selenium recovery process. Shown in Figure III-7 (page 1127) is a schematic of the tellurium recovery system. As can be seen in this diagram, TeO_2 goes through a series of pH adjustments to remove impurities. The first of these is a caustic leach designed to remove any residual copper. Another pH adjustment is performed to neutralize the tellurium bearing alkaline solution and precipitate tellurium as TeO_2. At this point, TeO_2 can be either marketed with no further refining or refined further through electrolysis to produce tellurium metal.

Wastewater generated in the tellurium processing cycle consists primarily of washing TeO_2 after precipitation with sulfuric acid. Spent electrolyte from electrolysis is normally in a closed loop with a preceding caustic leach step.

SUMMARY OF WASTEWATER SOURCES

In summary, the principal uses of water in the primary electrolyic copper refining subcategory are due to five processes:

1. Anode and cathode rinse water,
2. Spent electrolyte,
3. Casting contact cooling,
4. Casting scrubber, and
5. By-product recovery.

There are other wastewater streams associated with the refining of primary electrolytic copper. These wastewater streams include electrowinning arsine wet air pollution control, maintenance and cleanup water, and storm water runoff. These waste streams are not considered as a part of this rule making. EPA believes the flows and pollutant loadings associated with these waste streams are insignificant relative to the waste streams selected and are best handled by the appropriate permit authority on a case-by-case basis under the authority of Section 402 of the Clean Water

Act.

AGE, PRODUCTION, AND PROCESS PROFILE

The primary electrolytic copper industry consists of 14 refining operations. The location and discharge status of the primary electrolytic copper refining locations are shown in Figure III-8 (page 1128). In some cases both smelting and refining operations are found at or near the same site. As a rule, however, smelters are located near copper mines and mills in the Southwest, and electrolytic refineries are either found near smelters or near maritime centers.

Table III-1 (page 1119) shows the average age of the electrolytic refiners as 30 years. As seen in Table III-2 (page 1120) the average electrolytic refining plant production is 115,000 tons per year of electrolytic refined copper. The six electrolytic refineries processing anode slimes produce an average 11.5 million troy ounces of silver, 243,000 troy ounces of gold, 72,200 pounds of selenium, 221,000 pounds of tellurium, and 73,000 pounds of platinum and palladium per year.

As shown in Table III-1, there are three direct discharging and 11 zero discharging copper refiners. Table III-3 (page 1120) presents a summary of the number of facilities with a reported process and the number of facilities generating wastewater within that process. Table III-3 shows five facilities generating wastewater from electrolytic refining. All 14 primary electrolytic copper refineries considered in this rulemaking have the potential to discharge spent electrolyte. However, five of these plants generate wastewater by rinsing anodes when they are removed from the electrolytic cells.

TABLE III-1

INITIAL OPERATING YEARS (RANGE) SUMMARY OF PLANTS IN THE PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY BY DISCHARGE TYPE

	Electrolytic Copper Refining Plant Age Range (Years)								
	1983-1973	1972-1968	1967-1958	1957-1948	1947-1938	1937-1918	1917-1903	Before 1903	
Discharge Type	0-10	10-15	15-25	25-35	35-45	45-65	65-80	80- +	NR
Direct	-	1	2	-	-	-	-	-	-
Zero	2	-	1	2	-	1	1	-	4
Total	2	1	3	2	0	1	1	0	4

TABLE III-2

PRODUCTION RANGES FOR PRIMARY ELECTROLYTIC COPPER REFINING PLANTS

(tons/yr)

Production (1976) Range	Number of Copper Refiners
0 - 50000	3
50000 - 100000	2
100000 - 150000	0
150000 - 200000	2
200000 - Above	2
NR	5
TOTAL PLANTS	14

TABLE III-3

PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY SUMMARY OF PROCESSES AND ASSOCIATED WASTE STREAMS

Process	No. of Plants With Process	No. of Plants Reporting Generating Wastewater*
Electrolytic Refining	14	5
Casting	19	17
Casting Air pollution Control	3	1
By-Product Recovery	3	3

* Through reuse or evaporation practices, a plant may generate a wastewater from a particular process but not discharge it.

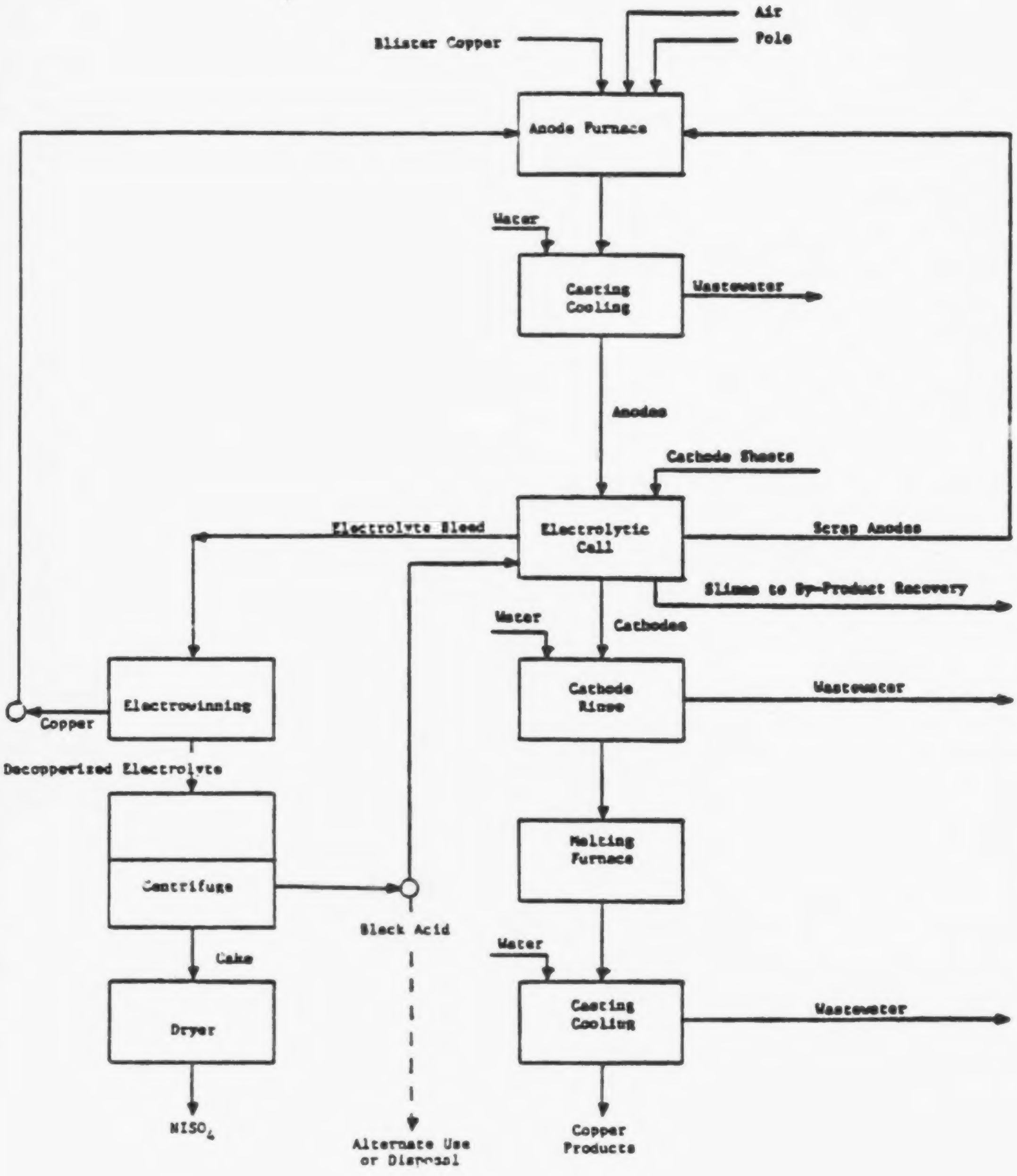
Air
Blister Copper
Pole
Anode Furnace
Water
Casting Cooling
Wastewater
Anodes
Cathode Sheets
Electrolyte Bleed
Electrolytic Cell
Scrap Anodes
Slimes to By-Product Recovery
Water
Cathodes
Electrowinning
Copper
Cathode Rinse
Wastewater
Decopperized Electrolyte
Melting Furnace
Centrifuge
Black Acid
Cake
Water
Dryer
Casting Cooling
Wastewater
NiSO$_4$
Alternate Use or Disposal
Copper Products

FIGURE III-1
PRIMARY ELECTROLYTIC COPPER REFINING PROCESS

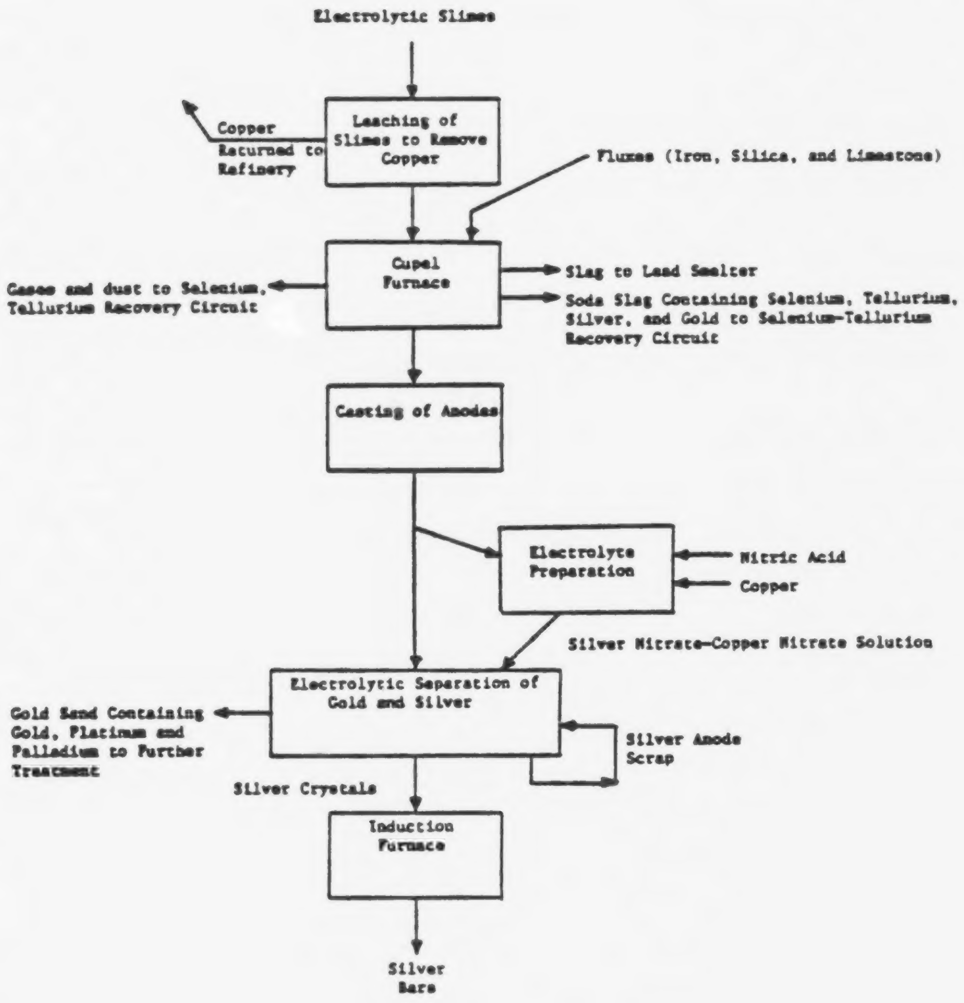
Electrolytic Slimes
Leaching of Slimes to Remove Copper
Copper Returned to Refinery
Fluxes (Iron, Silica, and Limestone)
Cupel Furnace
Slag to Lead Smelter
Gases and dust to Selenium, Tellurium Recovery Circuit
Soda Slag Containing Selenium, Tellurium, Silver, and Gold to Selenium-Tellurium Recovery Circuit
Casting of Anodes
Electrolyte Preparation
Nitric Acid
Copper
Silver Nitrate-Copper Nitrate Solution
Electrolytic Separation of Gold and Silver
Gold Sand Containing Gold, Platinum and Palladium to Further Treatment
Silver Anode Scrap
Silver Crystals
Induction Furnace
Silver Bars

FIGURE III-2
SILVER BY-PRODUCT RECOVERY PROCESS

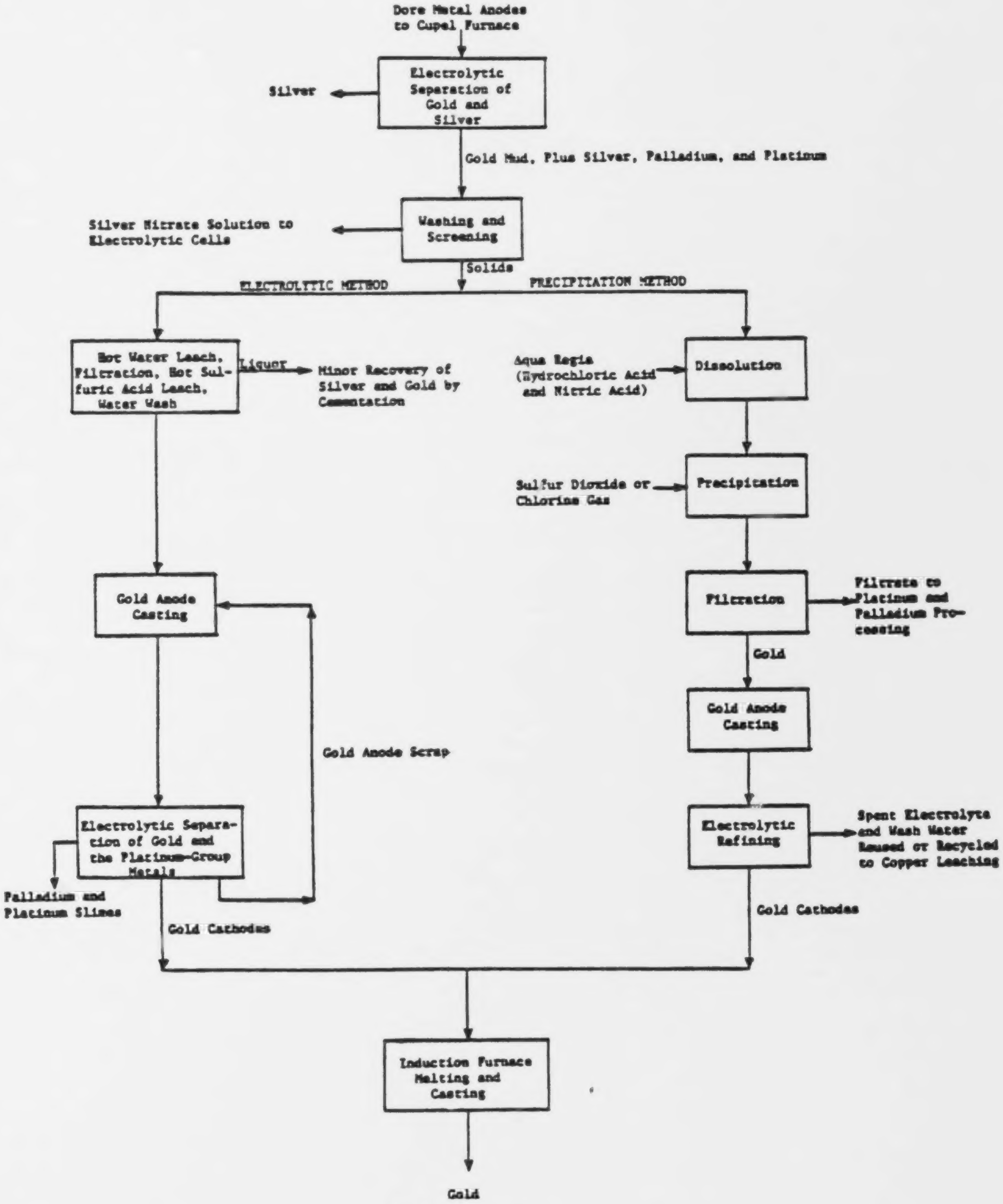
Dore Metal Anodes to Cupel Furnace
Electrolytic Separation of Gold and Silver
Silver
Gold Mud, Plus Silver, Palladium, and Platinum
Washing and Screening
Silver Nitrate Solution to Electrolytic Cells
Solids
ELECTROLYTIC METHOD
PRECIPITATION METHOD
Hot Water Leach, Filtration, Hot Sulfuric Acid Leach, Water Wash
Liquor
Minor Recovery of Silver and Gold by Cementation
Aqua Regia (Hydrochloric Acid and Nitric Acid)
Dissolution
Sulfur Dioxide or Chlorine Gas
Precipitation
Filtration
Filtrate to Platinum and Palladium Processing
Gold
Gold Anode Casting
Gold Anode Scrap
Gold Anode Casting
Electrolytic Separation of Gold and the Platinum-Group Metals
Palladium and Platinum Slimes
Gold Cathodes
Electrolytic Refining
Spent Electrolyte and Wash Water Reused or Recycled to Copper Leaching
Gold Cathodes
Induction Furnace Melting and Casting
Gold

FIGURE III-3
GOLD BY-PRODUCT RECOVERY PROCESS

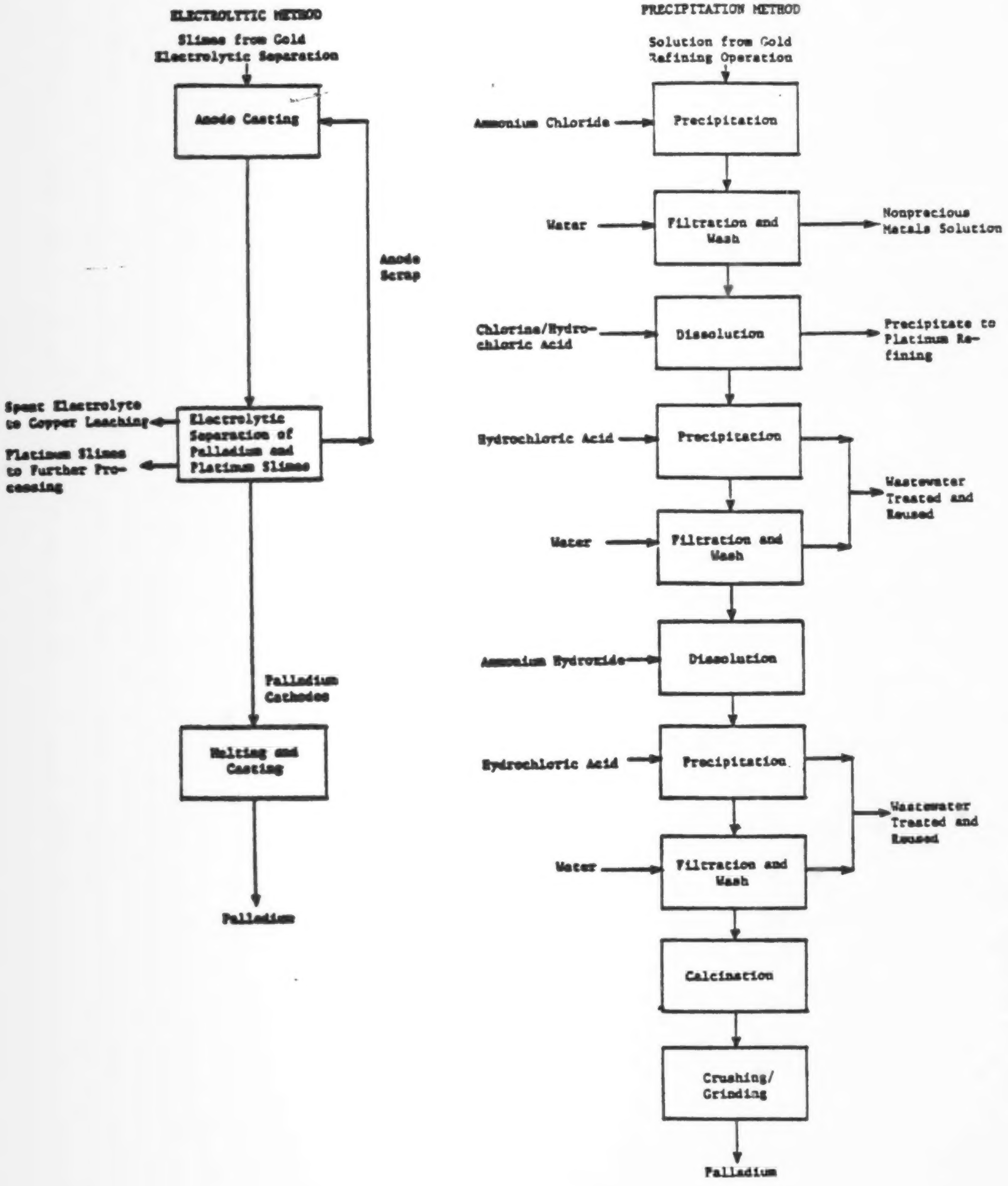
ELECTROLYTIC METHOD
Slimes from Gold Electrolytic Separation
Anode Casting
Anode Scrap
Spent Electrolyte to Copper Leaching
Electrolytic Separation of Palladium and Platinum Slimes
Platinum Slimes to Further Processing
Palladium Cathodes
Melting and Casting
Palladium
PRECIPITATION METHOD
Solution from Gold Refining Operation
Ammonium Chloride
Precipitation
Water
Filtration and Wash
Nonprecious Metals Solution
Chlorine/Hydrochloric Acid
Dissolution
Precipitate to Platinum Refining
Hydrochloric Acid
Precipitation
Wastewater Treated and Reused
Water
Filtration and Wash
Ammonium Hydroxide
Dissolution
Hydrochloric Acid
Precipitation
Wastewater Treated and Reused
Water
Filtration and Wash
Calcination
Crushing/Grinding
Palladium

FIGURE III-4
PALLADIUM BY-PRODUCT RECOVERY PROCESS

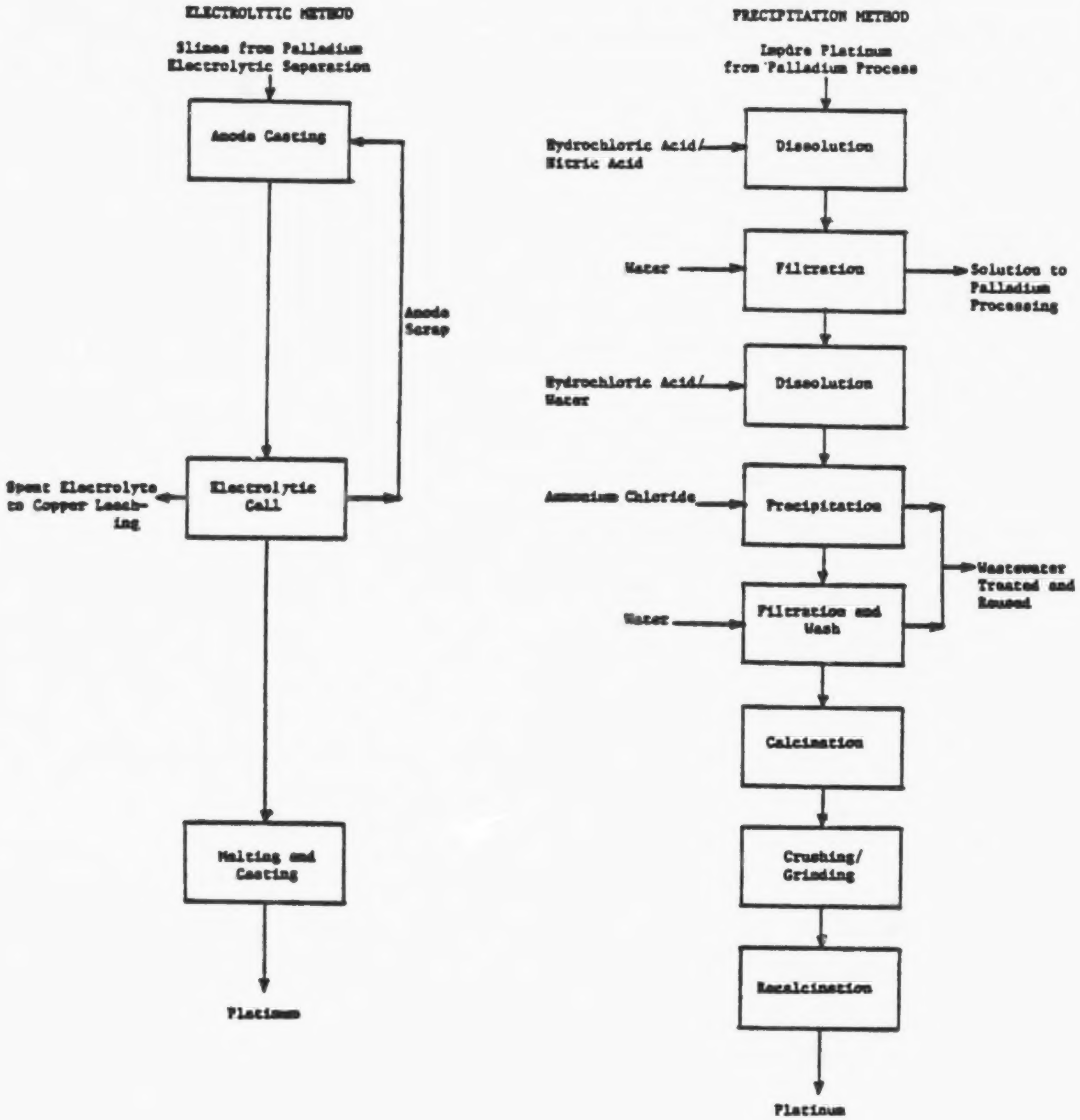
ELECTROLYTIC METHOD
Slimes from Palladium Electrolytic Separation
Anode Casting
Anode Scrap
Spent Electrolyte to Copper Leaching
Electrolytic Cell
Melting and Casting
Platinum
PRECIPITATION METHOD
Impure Platinum from Palladium Process
Hydrochloric Acid/ Nitric Acid
Dissolution
Water
Filtration
Solution to Palladium Processing
Hydrochloric Acid/ Water
Dissolution
Ammonium Chloride
Precipitation
Wastewater Treated and Reused
Water
Filtration and Wash
Calcination
Crushing/ Grinding
Recalcination
Platinum

FIGURE III-5
PLATINUM BY-PRODUCT RECOVERY PROCESS

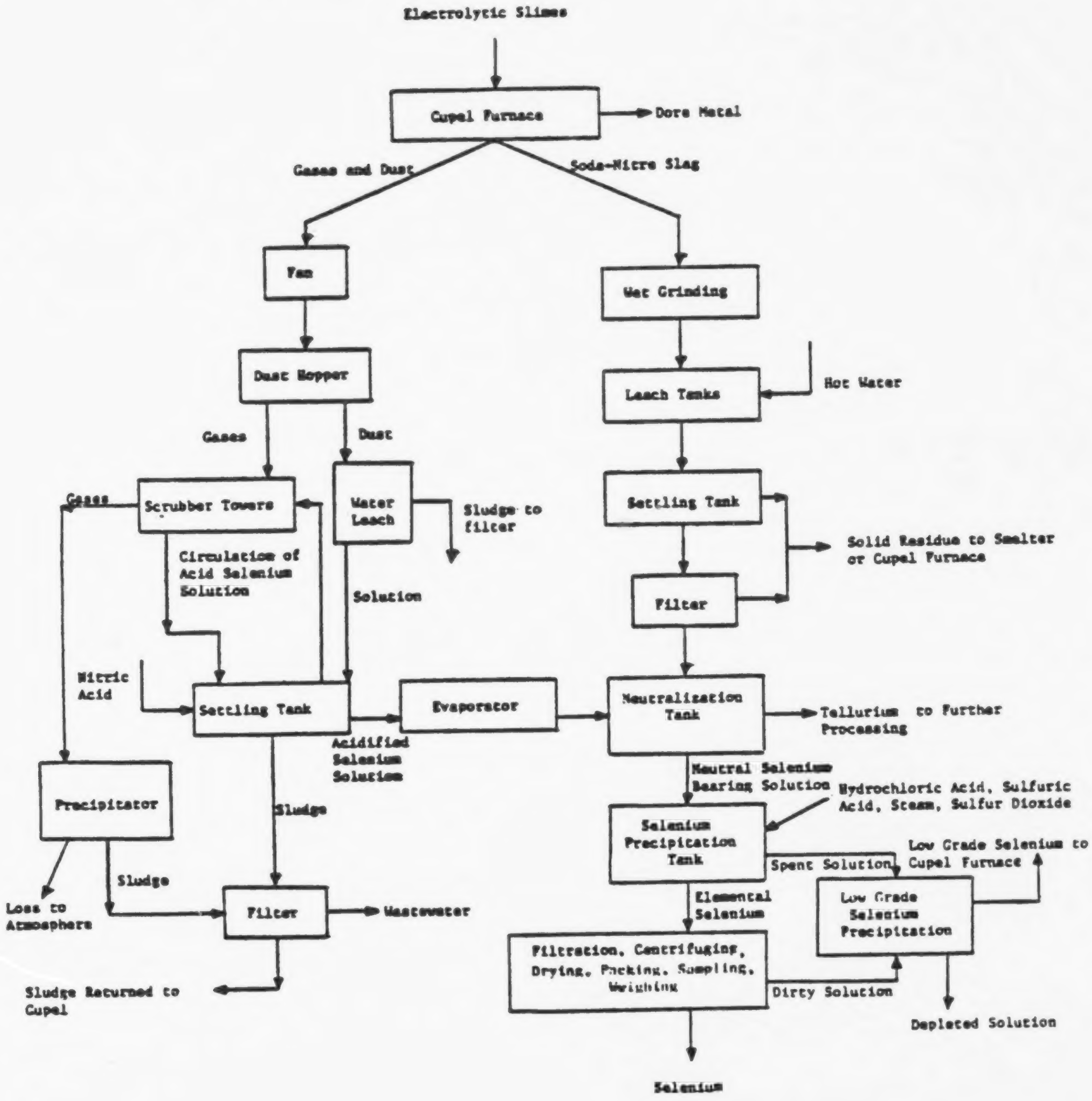
Electrolytic Slimes
Cupel Furnace
Dore Metal
Gases and Dust
Soda-Nitre Slag
Fan
Wet Grinding
Dust Hopper
Leach Tanks
Hot Water
Gases
Dust
Gases
Scrubber Towers
Water Leach
Sludge to filter
Settling Tank
Solid Residue to Smelter or Cupel Furnace
Circulation of Acid Selenium Solution
Solution
Filter
Nitric Acid
Settling Tank
Evaporator
Neutralization Tank
Tellurium to Further Processing
Acidified Selenium Solution
Neutral Selenium Bearing Solution
Hydrochloric Acid, Sulfuric Acid, Steam, Sulfur Dioxide
Precipitator
Sludge
Selenium Precipitation Tank
Low Grade Selenium to Cupel Furnace
Spent Solution
Sludge
Elemental Selenium
Low Grade Selenium Precipitation
Loss to Atmosphere
Filter
Wastewater
Filtration, Centrifuging, Drying, Packing, Sampling, Weighing
Sludge Returned to Cupel
Dirty Solution
Depleted Solution
Selenium

FIGURE III-6
SELENIUM BY-PRODUCT RECOVERY PROCESS

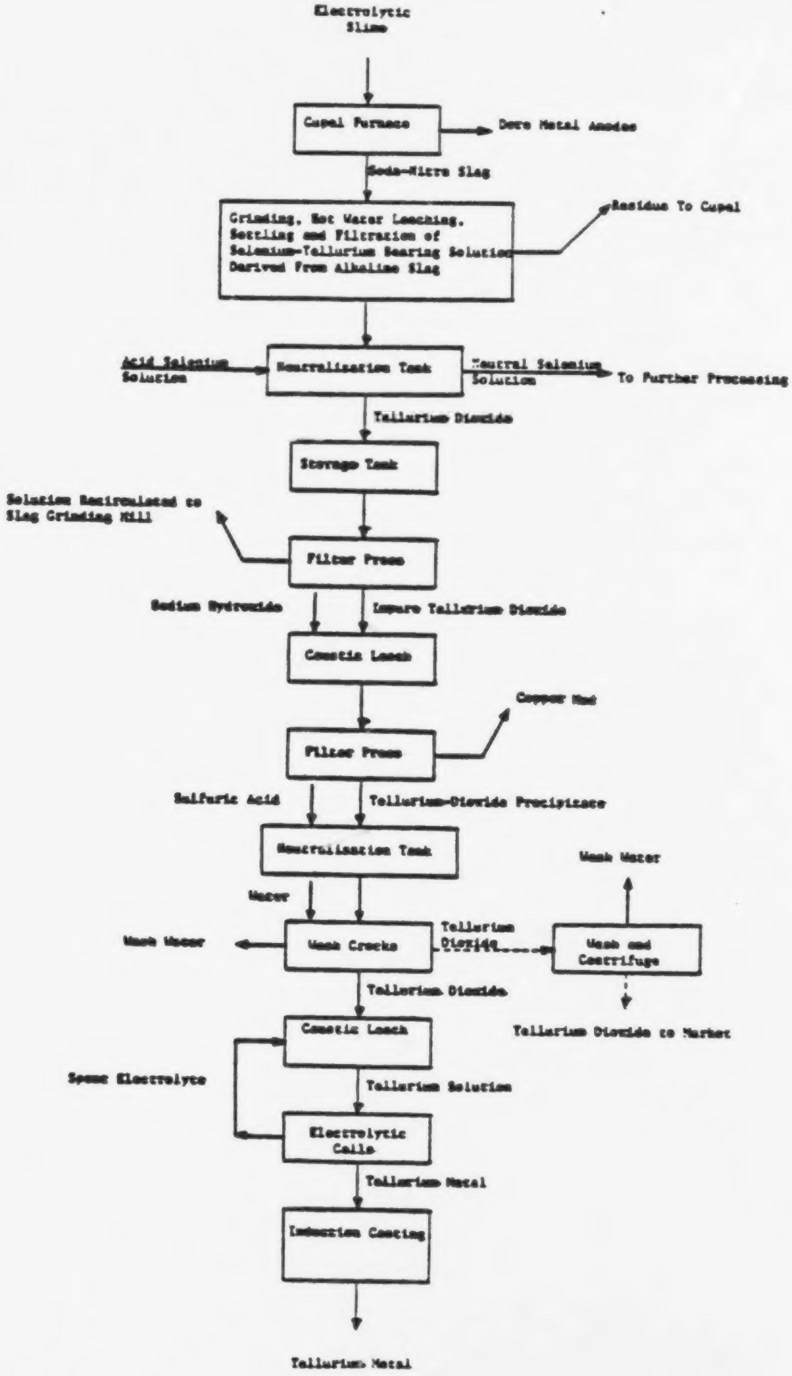
Electrolytic Slime
Cupel Furnace
Dore Metal Anodes
Soda-Nitre Slag
Grinding, Hot Water Leaching, Settling and Filtration of Selenium-Tellurium Bearing Solution Derived From Alkaline Slag
Residue To Cupel
Acid Selenium Solution
Neutralization Tank
Neutral Selenium Solution
To Further Processing
Tellurium Dioxide
Storage Tank
Solution Recirculated to Slag Grinding Mill
Filter Press
Sodium Hydroxide
Impure Tellurium Dioxide
Caustic Leach
Copper Mud
Filter Press
Sulfuric Acid
Tellurium-Dioxide Precipitate
Neutralization Tank
Wash Water
Water
Wash Water
Wash Crocks
Tellurium Dioxide
Wash and Centrifuge
Tellurium Dioxide
Tellurium Dioxide to Market
Caustic Leach
Spent Electrolyte
Tellurium Solution
Electrolytic Cells
Tellurium Metal
Induction Casting
Tellurium Metal

FIGURE III-7
TELLURIUM BY-PRODUCT RECOVERY PROCESS

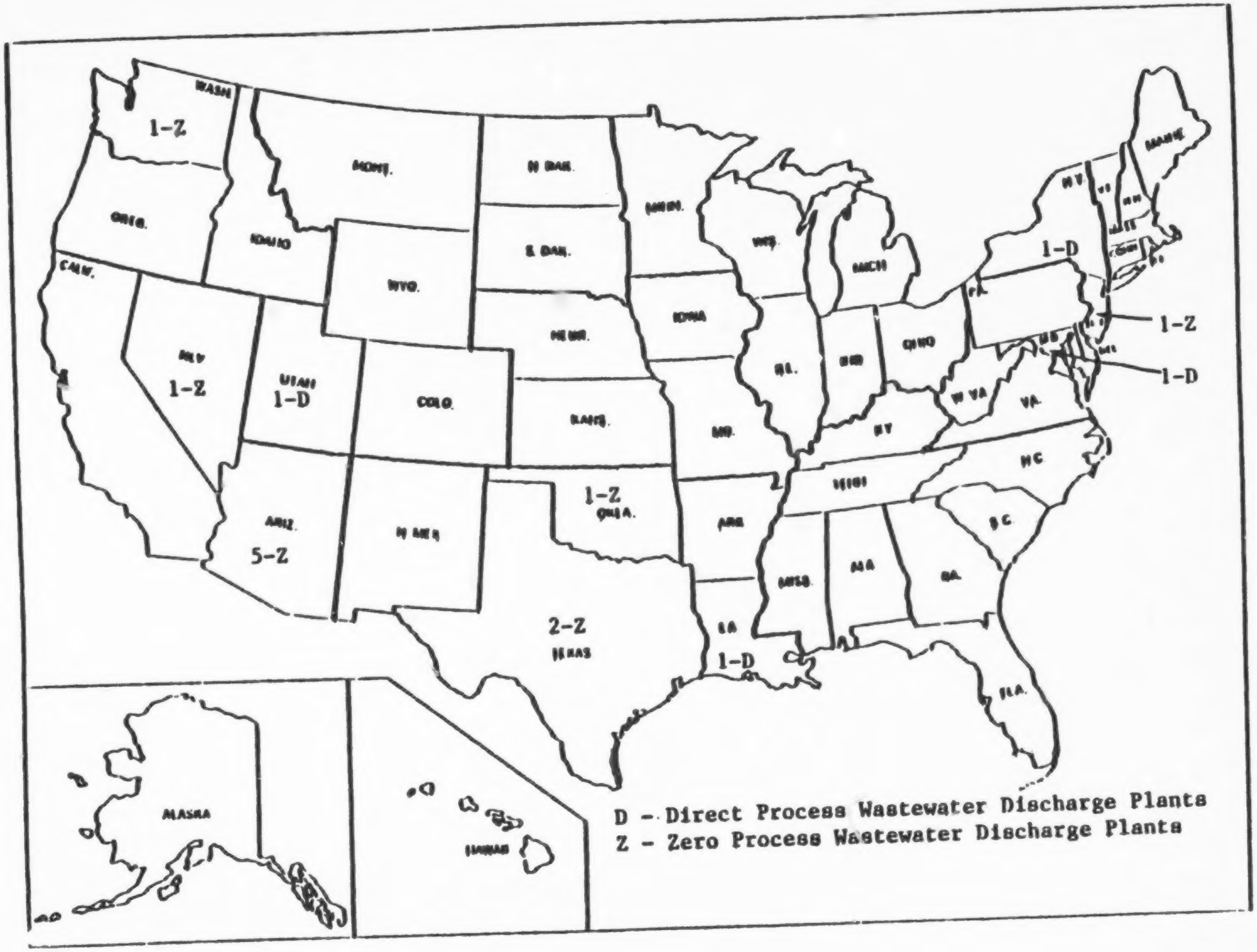
WASH.
1-Z
ORE.
CALIF.
IDAHO
MONT.
NEV
1-Z
UTAH
1-D
WYO.
COLO.
ARIZ.
5-Z
N MEX
N DAK.
S DAK.
NEBR.
KANS.
OKLA.
1-Z
TEXAS
2-Z
MINN.
IOWA
MO.
ARK.
LA
1-D
WIS.
ILL.
MICH
IND
OHIO
KY
TENN
MISS.
ALA
GA.
FLA.
S C.
N C
VA.
W VA
PA.
NY
1-D
1-Z
1-D
MAINE
ALASKA
HAWAII
D - Direct Process Wastewater Discharge Plants
Z - Zero Process Wastewater Discharge Plants

FIGURE III-8

GEOGRAPHIC LOCATIONS OF PRIMARY ELECTROLYTIC COPPER PLANTS

SECTION IV

SUBCATEGORIZATION

This section summarizes the factors considered during the designation of the primary electrolytic copper refining subcategory and its related building blocks.

Primary electrolytic copper refiners located onsite with primary copper smelters were considered as a single subcategory during the previous 1975 rulemaking. Primary copper refiners not located with smelters were considered as a separate subcategory. That rulemaking established interim BPT and BAT limitations, along with NSPS and PSNS for the primary copper subcategory. In 1980, a modified BPT regulation was promulgated for the primary copper subcategory that divided smelting and refining into two separate subcategories regardless of location. The rational for this 1980 subcategorization was detailed as part of that rulemaking.

FACTORS CONSIDERED IN SUBDIVIDING THE PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

The factors listed for general subcategorization were each evaluated when considering subdivision of the primary electrolytic copper refining subcategory. In the discussion that follows, the factors will be described as they pertain to this particular subcategory.

The rationale for considering further subdivision of the primary electrolytic copper refining subcategory is based primarily on the production process used. Within this subcategory, a number of different operations are performed, which may or may not have a water use or discharge, and which may require the establishment of separate effluent limitations. Since primary electrolytic copper refining is a single subcategory, a thorough examination of the production processes, water use and discharge practices, and pollution generation rates has illustrated the need for limitations and standards based on a specific set of waste streams. Possible sources of wastewater from an electrolytic refiner include these subdivisions or building blocks:

1. Anode and cathode rinse,
2. Spent electrolyte,
3. Casting contact cooling,
4. Casting wet air pollution control, and
5. By-product recovery.

A number of other factors considered in this evaluation supported the establishment of the five subdivisions or were shown to be inappropriate bases for primary copper refining subcategorization. These are discussed briefly below.

RAW MATERIALS

The principle raw material for electrolytic copper refining is fire refined blister copper from a copper smelter. Blister copper is approximately 98 percent pure copper with slight impurities of nickel, thallium, selenium, and precious metals. These raw materials warrant subcategorization for primary electrolytic copper refining separate from the production of other metals. In addition, no factors pertaining to raw materials have been identified that affect the ability of plants in the primary copper electrolytic refining subcategory to achieve effluent limitations.

PLANT SIZE

A review of the 14 copper refining plants who reported sufficient information showed that two plants have capacities of less than 90,000 metric tons (100,000 short tons) per year, four plants have capacities between 90,000 and 180,000 metric tons (100,000 and 200,000 short tons) per year, and two plants have capacities greater than 180,000 metric tons (200,000 short tons) per year.

No factors relating to this distribution of plant size and pertaining to a given plant's ability to achieve effluent limitations have been identified.

PLANT AGE

Primary copper smelting and electrolytic refining is a relatively new industrial process which evolved as a result of the availability of electricity in large quantities. Through the past century, new methods for manufacturing copper have developed which may combine several of the traditional smelting steps into one. In addition, new advances have been made in hydrometallurgical processes to handle copper oxide ore. These newer processes, however, are simply subsets of the older smelting or refining processes in terms of wastewater generated. Therefore, the oldest plants built in the early 1900's are fundamentally equivalent to those built today. As a result, neither the concentration of constituents in wastewater nor the capability to meet limitations is related to plant age. Because of the general uniformity of copper process technology, the application of most wastewater treatment systems is dependent on factors other than age.

Through the years, electrolytic copper refining has not changed dramatically. The same chemical principles used in the early 1900's are still practiced today. New advances in this area have been primarily in the development of automated methods to mechanically handle intermediate and final products. Neither the concentration of constituents in wastewater nor the effluent performance attainable is related to plant age.

PRODUCT

Product is a good reason for subdividing the primary copper operations from production of other metals since manufacturing operations and wastewater characteristics are usually unique for a particular product. The end result of primary copper refining is cathode copper, 99.99 percent pure copper, which may be cast or marketed with no further processing. From the survey taken of primary copper producers, 40 percent of the smelting facilities also contain electrolytic refining facilities onsite. This indicates that a substantial amount of primary copper electrolytic refining is a subset of the copper integrated manufacturing operations. Therefore, product cannot be considered as a means of subdividing primary copper smelting from refining.

PRODUCTION NORMALIZING PARAMETERS

As discussed previously, the effluent limitations and standards developed in this document establish mass limitations on the discharge of specific pollutant parameters. To allow this regulation to be applied to plants with various production capacities, the mass of pollutant discharge must be related to a unit of product. This factor is known as the production normalizing parameter (PNP). In general, the amount of copper produced by the respective manufacturing process is used as the PNP. This is based on the principle that the amount of water generated is proportional to the amount of product made. For primary electrolytic copper refining, actual production has been selected as the PNP for all of the subdivisions as shown below:

Subdivision	PNP
1. Anode and cathode rinse water	kkg of cathode copper produced
2. Spent electrolyte	kkg of cathode copper produced
3. Casting contact cooling	kkg of copper cast
4. Casting wet air pollution control	kkg of copper cast
5. By-product recovery	kkg of by-product recovered from electrolytic slimes processing

Other PNPs were considered for certain subdivisions; however, they were rejected and are discussed below.

ANODE AND CATHODE RINSE WATER

The production normalizing parameter selected for this subdivision is cathode copper produced. Capacity, rather than actual production, was considered for use as the production normalizing parameter. When analytical samples were taken, however, the pollutant concentration calculations were based on actual measured flows and production rates. In order to be consistent when determining pollutant loadings, the cathode copper production was chosen. Use of actual production also eliminates the need for plants to reduce water flow during years in which actual production is greater than design capacity.

The casting production was also considered as a production normalizing parameter. This production cannot be used because not all cathode copper is cast before marketing.

SPENT ELECTROLYTE

The production normalizing parameter for spent electrolyte is also cathode copper. For those same reasons discussed above, electrolytic capacity and casting production were not chosen as production normalizing parameters. This preserves the relationship between the sampling data and the rates at the time of sampling.

CASTING CONTACT COOLING

The production normalizing parameter chosen for this process is actual casting production. Cathode production from the electrolytic tank house cannot be used because not all electrolytic copper is cast before leaving the plant. To preserve the relationship between sampling data and production, the casting capacity could not be used as discussed earlier.

CASTING WET AIR POLLUTION CONTROL

To control air emissions from a furnace, wet air pollution methods may be used. The production normalizing parameter has been chosen as actual casting production instead of capacity. Originally it was thought that capacity might be a more appropriate measure than actual production because water use in the scrubber is independent of production. Consistency in the application of sampling data, however, necessitated the use of casting production as the production normalizing parameter. This will ensure that higher capacity utilization will not reduce the production normalized flow allowance from this operation.

BY-PRODUCT RECOVERY

The production normalizing parameter chosen for the recovery of nickel sulfate and precious metals is actual production of these materials. As an alternative, cathode copper was considered as the production normalizing parameter, but this does not allow for a difference in the quantities of impurities contained within anode copper. Furthermore, for consistency, the final product and not an intermediate was chosen as the PNP.

SECTION V

WATER USE AND WASTEWATER CHARACTERISTICS

This section describes the characteristics of wastewater associated with the primary electrolytic copper refining subcategory. Data used to quantify wastewater flow and pollutant concentrations are presented, summarized, and discussed. The contribution of specific production processes to the overall wastewater discharge from primary copper refining plants is identified whenever possible.

Two principal data sources were used in the development of effluent limitations and standards for this subcategory: data collection portfolios and field sampling results. Data collection portfolios, completed for the primary copper refining subcategory, contain information regarding wastewater flows and production levels.

Since the data collection portfolios were collected, the Agency has learned that two primary copper electrolytic refiners have shut down. Flow and production data from these plants are still included in this section and in the remainder of the document. Analytical data gathered at one of the plants are also presented. Although these plants are closed, flow and production data from the plants are an integral part of the flow components of the BAT effluent mass limitations because these plants remain representative of flow and production rates in this industry. The Agency believes that these data provide useful measures of the relationship between production and wastewater discharge. In light of this conclusion, EPA is using these data in its consideration of BAT performance. Therefore, it is necessary to present this information so that the limitations are documented.

Additionally, the Agency received updated and revised flow and production data for some waste streams through comments on the proposed regulation and through special requests. These data are also included in this section.

In order to quantify the pollutant discharge from primary copper electrolytic refining plants, a field sampling program was conducted. Wastewater samples were collected in two phases: screening and verification. The first phase, screen sampling, was to identify which toxic pollutants were present in the wastewaters from production of the various metals. Screening samples were analyzed for 125 of the 126 toxic pollutants and other pollutants deemed appropriate. Because the analytical standard for TCDD was judged to be too hazardous to be made generally available, samples were never analyzed for this pollutant. There is no reason to expect that TCDD would be present in primary copper electrolytic refining wastewater. A total of 10 plants were selected for screen sampling in the nonferrous metals manufacturing category. A complete list of the pollutants considered and a summary of the techniques used in sampling and laboratory analyses are included in Section V of Vol. 1. In general, the samples were analyzed for three classes of pollutants: toxic organic pollutants, toxic metal pollutants, and criteria pollutants (which includes both conventional and nonconventional pollutants).

As described in Section IV of this supplement, the primary copper electrolytic refining subcategory has been further categorized into five building blocks. This regulation contains mass discharge limitations and standards for five unit processes discharging process wastewater. Differences in the wastewater characteristics associated with these subdivisions are to be expected. For this reason, wastewater streams corresponding to each subdivision are addressed separately in the discussions that follow.

WASTEWATER SOURCES, DISCHARGE RATES, AND CHARACTERISTICS

The wastewater data presented in this section were evaluated in light of production process information compiled during this study. As a result, it was possible to identify the principle wastewater sources in the primary electrolytic copper refining subcategory. These include:

1. Anode and cathode rinse water,
2. Spent electrolyte,
3. Casting contact cooling water,
4. Casting wet air pollution control, and
5. By-product recovery.

Data supplied by dcp responses were used to calculate the amount of water used and discharged per metric ton of production. The two ratios calculated are differentiated by the flow rate used in the calculation. Water use is defined as the volume of water of other fluid (e.g., electrolyte) required for a given process per mass of copper product and is therefore based on the sum of recycle and make-up flows to a given process. Wastewater flow discharged after pretreatment or recycle (if these are present) is used in calculating the production normalized flow--the volume of wastewater, discharged from a given process to further treatment, disposal, or discharge per mass of copper produced. Differences between the water use and wastewater flows associated with a given stream result from recycle, evaporation, and carry over on the product. The production values used in calculations correspond to the production normalizing parameter, PNP, assigned to each stream, as outlined in Section IV. The production normalized flows were compiled and statistically analyzed by stream type. Where appropriate, an attempt was made to identify factors that could account for variations in water use. This information is summarized in this section. A similar analysis of factors affecting the wastewater values is presented in Sections X, XI, and XII where representative BAT, BDT and pretreatment discharge flows are selected for use in calculating the effluent limitations. As an example, anode and cathode rinse wastewater flow is related to the cathode copper production. As such, the discharge rate is expressed in liters of rinse wastewater per metric ton of cathode copper production (gallons of rinse water per ton of cathode copper production).

Characteristics of wastewater from the previously listed processes were determined from sampling data collected at primary copper refiners. These data were used in two ways. First, pollutants were selected for regulation based on the sampling data. Secondly, the sampling data was used to estimate the yearly mass of pollutant generated by each waste stream for the entire industry. There were four site visits at two refiners, which represents 14 percent of the copper refiners. Diagrams indicating the sampling sites and contributing production processes are shown in Figures V-1 and V-2 (pages 1150 and 1151).

In the data collection portfolios, plants were asked to indicate whether or not any of the toxic pollutants were believed to be present in their wastewater. Responses for the toxic metals selected as pollutant parameters are summarized below for those plants responding to that portion of the questionnaire. Results of the responses from facilities with electrolytic refining only and facilities having both smelting and electrolytic refining are shown in Table V-1 (page 1139). These responses demonstrate that primary copper refinery facilities know that process wastewater contains quantifiable concentrations of toxic metal pollutants.

The raw wastewater sampling data for the primary copper refining subcategory is presented in Tables V-5 and V-6 (pages 1143 and 1144). Treated wastewater sampling data are shown in Table V-7 (page 1145). The stream codes displayed in Tables V-5 through V-7 may be used to identify the location of each of the samples on the process flow diagrams in Figures V-1 and V-2. Where no data are listed for a specific day of sampling, the wastewater samples for the stream were not collected. If the analyses did not detect a pollutant in a waste stream, the pollutant was omitted from the table.

The data tables included some samples measured at concentrations considered not quantifiable. The base neutral extractable, acid extractable, and volatile toxic organics generally are considered not quantifiable at concentrations equal to or less than 0.010 mg/l. Below this concentration, organic analytical results are not quantitatively accurate; however, the analyses are useful to indicate the presence of a particular pollutant. The pesticide fraction is considered not quantifiable at concentrations equal to or less than 0.005 mg/l. Nonquantifiable results are designated in the tables with an asterisk (double asterisk for pesticides).

These detection limits shown on the data tables are not the same in all cases as the published detection limits for these pollutants by the same analytical methods. The detection limits used were reported with the analytical data and hence are the appropriate limits to apply to the data. Detection limit variation can occur as a result of a number of laboratory-specific, equipment-specific, and daily operator-specific factors. These factors can include day-to-day differences in machine calibration, variation in stock solutions, and variation in operators.

The statistical analysis of data includes some samples measured at concentrations considered not quantifiable. Data reported as an asterisk are considered as detected but below quantifiable concentrations, and a value of zero is used for averaging. Toxic organic, nonconventional, and conventional pollutant data reported with a "less than" sign are considered as detected but not further quantifiable. A value of zero is also used for averaging. If a pollutant is reported as not detected, it is excluded in calculating the average. Finally, toxic metal values reported as less than a certain value were considered as not detected and a value of zero is used in the calculation of the average. For example, three samples reported as ND, *, and 0.021 mg/l have an average value of 0.010 mg/l. The averages calculated are presented with the sampling data. These values were not used in the selection of pollutant parameters.

In the following discussion, water use and field sampling data are presented for each operation. Appropriate tubing or background blank and source water concentrations are presented with the summaries of the sampling data. Figures V-1 through V-4 show the location of wastewater sampling sites at each facility. The method by which each sample was collected is indicated by number, as follows:

1. one-time grab
2. 24-hour manual composite
3. 24-hour automatic composite
4. 48-hour manual composite
5. 48-hour automatic composite
6. 72-hour manual composite
7. 72-hour automatic composite

COPPER REFINING WASTEWATER SOURCES AND CHARACTERISTICS

Presented below is a discussion of the characteristics of the significant wastewater sources attributable to the refining of copper.

Anode and Cathode Rinse Water

Cathodes and anodes removed from electrolytic cells are often rinsed before further processing. The waste rinse water is characterized by significant concentrations of toxic metal pollutants such as nickel (4,200 mg/l) and zinc (32 mg/l). These pollutants are a result of impurities in the anodes that are released into the electrolyte. Table V-5 summarizes the field sampling data for the toxic and selected conventional and nonconventional pollutants detected in wastewater from a cathode rinsing operation.

Of the six plants who reported rinsing anodes and cathodes, only one discharges spent rinse water. The production normalized flow calculated for this plant is 552 liters per metric ton (l/kkg) of cathode copper produced (132 gal/ton).

Spent Electrolyte

To maintain a correct electrolytic balance during refining, a slip stream of electrolyte is continuously removed for purification. There are two plants in the primary copper electrolytic refining subcategory who discharge this stream after purification. Table V-2 (page 1140) illustrates the volumes of electrolyte used and discharged on a production basis for these two plants.

Spent electrolyte from an electrowinning process is characterized by significant concentrations of toxic metal pollutants such as nickel (4,200 mg/l) and zinc (32 mg/l). These toxic metals are a result of impurities present in anodes and are released into the electrolyte during refining. These pollutants are soluble in the electrolyte and are not removed during electrowinning. Table V-5 (page 1143) presents the sampling data gathered from this operation.

Casting Contact Cooling Water

There are two types of casting that can take place at a copper refiner. Partially consumed anode butts from the refining process are removed in monthly cycles for recasting, and cathode copper is cast into usable shapes for forming processes. The Agency collected one raw wastewater sample from a smelter casting operation. Wastewater samples collected at this site indicate casting contact cooling water contains low concentrations of toxic metals. As might be expected, the significant toxic pollutant found in wastewater from a casting operation is copper. As can be seen in Table V-6 (page 1144), sampling data from this site found the copper concentration as 1.6 mg/l. Table V-3 (page 1141) illustrates the water usage and discharge rates on a production basis for casting contact cooling water.

Casting Furnace Scrubber Liquor

There was one facility that reported controlling emissions from a furnace with a wet air pollution control system. This facility reported a production normalized water usage and discharge rate of 16 liters per metric ton of copper cast (3.8 gal/ton). The Agency did not collect any raw wastewater samples from furnace scrubbing operations. The water quality characteristics of this waste stream are expected to be very similar to casting contact cooling. Loadings of toxic metal pollutants will be slightly lower than those found in casting contact cooling, while the level of suspended solids is expected to be higher in furnace scrubber water.

By-Product Recovery

The recovery of precious and base metals is done through a series of smelting, leaching, precipitation, and electrolytic refining processes. In several of the leaching, precipitation, and filtration steps, there is the potential of discharge of leachate, supernatant, and filtrate. These waste streams are expected to contain toxic metal pollutants. Some plants recycle this wastewater within the by-product recovery process or treat and reuse the water in other plant processes. Wastewater from scrubbers on cupel furnaces, drying furnaces, and precipitation steps contains precious and base metals that can be recovered. Wastewater from these scrubbers is used as makeup water within the by-product recovery process or treated and used in other plant processes. In addition, the electrolytic media are also a potential source of wastewater. Spent leaching solutions and discarded supernatant may contain such toxic metal pollutants as copper, arsenic, lead, and nickel. Spent electrolyte from silver electrolytic refining and gold electrolytic refining consists of silver nitrate, silver chloride, and copper nitrate. Spent electrolyte may become a waste stream after the silver and copper are removed from the solutions through cementation. Spent electrolyte from palladium and platinum electrolytic refining is also a potential wastewater source. However, one plant reports sending this wastewater to the copper slimes leaching operation for reprocessing. Contact cooling water used in casting dore anodes is discharged to a wastewater treatment system at one plant. However, the Agency believes there is no need to treat casting contact cooling water from by-product recovery. EPA sampled casting contact cooling water from similar operations at a secondary precious metals plant in the nonferrous metals manufacturing category. The pollutant loadings in this wastewater are insignificant compared with the other waste streams selected. (The sampling data are presented in the secondary precious metals subcategory supplement.)

One plant operates a wet scrubber on fusion kilns to control sulfur dioxide (SO_2) in the kiln off-gases. The scrubber water is not recycled but is discharged to the plant wastewater treatment system. However, the scrubber wastewater flow rate comprises less than one percent of the total plant regulatory flow. Table V-4 (page 1142) presents the volumes of wastewater generated during by-product recovery.

TABLE V-1

INDICATED PRESENCE OR ABSENCE OF TOXIC METAL POLLUTANTS DCP DATA

For plants having electrolytic refining only

	Known Present	Believed Present	Believed Absent	Known Absent
Antimony	2	1	2	0
Cadmium	2	1	2	0
Chromium	1	3	1	0
Copper	5	0	0	0
Lead	3	1	1	0
Nickel	4	0	1	0
Selenium	2	2	1	0
Zinc	3	2	0	0

For plants having both smelting and refining

	Known Present	Believed Present	Believed Absent	Known Absent
Antimony	4	1	2	0
Cadmium	4	1	2	0
Chromium	4	0	3	0
Copper	7	0	0	0
Lead	5	1	1	0
Nickel	4	2	1	0
Selenium	4	2	1	0
Zinc	5	2	0	0

TABLE V-2

ELECTROLYTE USE AND SPENT ELECTROLYTE DISCHARGE RATES FOR CATHODE COPPER PRODUCTION

(l/kkg of cathode copper refined)

Plant Code	Percent Recycle	Production Normalized Electrolyte Use (l/kkg)	(gal/ton)	Production Normalized Discharge Flow (l/kkg)	(gal/ton)
214	NR	NR	NR	48.9	11.73
216(a)	99	1182.5	283.0	11.5	2.75
62	100	NR	NR	0	0
60	100	NR	NR	0	0
201	100	NR	NR	0	0
202(b)	100	NR	NR	0	0
206	100	NR	NR	0	0
203	NR	NR	NR	NR	NR
205(c)	0	NR	NR	8.7	2.08
211(a)	0	NR	NR	NR	NR
215	NR	NR	NR	NR	NR
217(d)	0	NR	NR	260	62.4
218	NR	NR	NR	NR	NR
7000	NR	NR	NR	NR	NR

NR - Present, but not reported in dcp.
(a) - Spent electrolyte is ultimately evaporated.
(b) - Plant closed.
(c) - Deep well injection, no electrowinning.
(d) - Sold as copper sulfate, no electrowinning.

TABLE V-3

WATER USE AND DISCHARGE RATES FOR CASTING CONTACT COOLING

(l/kkg of copper cast)

Plant	Percent recycle	Production Normalized Water Use (l/kkg)	Production Normalized Water Use (gal/ton)	Production Normalized Discharge Flow (l/kkg)	Production Normalized Discharge Flow (gal/ton)
202(a)	0	15273	3655	15273	3655
214(b)	0	2298	550	2298	550
215	98	46592	11150	932	223
216	98	26325	6300	526	126
214	NR	NR	NR	137	33
217	93	555	133	29	7
62	100	NR	NR	0	0
206	100	NR	NR	0	0
205	NR	NR	NR	NR	NR
211	NR	NR	NR	NR	NR

NR -- Data not reported in dcp

(a) -- Plant closed

(b) -- Plant operates two casting operations

TABLE V-4

WATER USE AND DISCHARGE RATES FOR BY-PRODUCT RECOVERY

(l/kkg of total by-product)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
62	100	2620	0
205	0	4902	0*
206!	NR	NR	NR
211	NR	NR	NR
214	NR	NR	94318
216!	100	1533647	0

! -- Facility no longer operates by-product recovery

* -- Wastewater disposed through deep well disposal

NR-- Data not reported in dcp

TABLE V-5

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA
REFINING SPENT ELECTROLYTE AND CATHODE WASH
RAW WASTEWATER

Pollutants	Stream Code	Sample Type†	Source(b)	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
114. antimony	222	1		0.4			0.4
115. arsenic	222	1		120			120
117. beryllium	222	1		< 0.2			< 0.2
118. cadmium	222	1		< 0.03			< 0.03
119. chromium	222	1		0.76			0.76
120. copper	222	1		3.9			3.9
122. lead	222	1		1.4			1.4
123. mercury	222	1		< 0.0005			< 0.0005
124. nickel	222	1		4200			4200
126. silver	222	1		0.13			0.13
128. zinc	222	1		31.5			31.5
Nonconventionals							
total organic carbon (TOC)	222	1		370			370
Conventionals							
total suspended solids (TSS)	222	1		1140			1140
pH (standard units)	222	1		1.2			

(a) This sample was not analyzed for toxic organics.

(b) Source water for this plant was not sampled.

† Sample type. Note: These numbers also apply to subsequent sampling data tables in this section.

1 - one-time grab
2 - 24-hour manual composite
3 - 24-hour automatic composite
4 - 48-hour manual composite
5 - 48-hour automatic composite
6 - 48-hour manual composite
7 - 72-hour automatic composite

* Indicates less than or equal to 0.01 mg/l.
** Indicates less than or equal to 0.005 mg/l.

TABLE V-6

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA
FIRE REFINED COPPER CASTING CONTACT COOLING WATER
RAW WASTEWATER

Pollutants	Stream Code	Sample Type	Source(b)	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
114. antimony	216	1		< 0.050			< 0.050
115. arsenic	216	1		< 0.002			< 0.002
117. beryllium	216	1		< 0.002			< 0.002
118. cadmium	216	1		< 0.020			< 0.020
119. chromium	216	1		< 0.024			< 0.024
120. copper	216	1		1.61			1.61
122. lead	216	1		< 0.060			< 0.060
123. mercury	216	1		< 0.0005			< 0.0005
124. nickel	216	1		< 0.005			< 0.05
125. selenium	216	1		0.015			0.015
126. silver	216	1		< 0.025			< 0.025
127. thallium	216	1		< 0.100			<0.100
128. zinc	216	1		0.052			0.052
Nonconventionals							
chemical oxygen demand (COD)	216	1		< 2			< 2
total organic carbon (TOC)	216	1		7			7
Conventionals							
total suspended solids (TSS)	216	1		18			18
pH (standard units)	216	1		7.6			

(a) This sample was not analyzed for toxic organic pollutants.

(b) Source water for this plant was not sampled.

TABLE V-7

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
1. acenaphthene	55	1	ND	ND	*	ND	*
	90	2	ND	0.016	ND	ND	0.016
4. benzene	55	3	ND	*	*	ND	*
6. carbon tetrachloride	90	2	ND	ND	0.02	ND	0.02
11. 1,1,1-trichlorethane	55	1	ND	ND	*	*	*
15. 1,1,2,2-tetrachloroethane	55	1	ND	ND	*	*	*
23. chloroform	55	1	0.057	*	*	0.057	0.019
	90	2	ND	ND	0.012	*	0.006
25. 1,2-dichlorobenzene	55	1	ND	ND	ND	ND	
	90	2	ND	ND	0.076	0.046	0.061
29. 1-1-dichloroethylene	55	1	ND	*	*	ND	*
	90	2	ND	0.034	ND	ND	0.034
30. 1-2,trans-dichloroethylene	55	1	ND	*	*	*	*
39. fluoranthene	55	3	ND	ND	*	ND	*
	90	2	ND	*	*	0.017	0.006
55. naphthalene	55	3	ND	ND	*	ND	*
	90	2	ND	ND	ND	ND	
66. bis(2-ethylhexyl) phthalate	55	3	7.16	2.21	1.20	0.096	1.17
	90	2	0.036	0.032	0.041	0.024	0.032
67. butyl benzyl phthalate	55	3	*	*	ND	0.051	0.026
	90	2	ND	*	0.011	*	0.004
68. di-n-butyl phthalate	55	3	*	*	0.075	*	0.025
	90	2	*	*	0.012	*	0.004
9. di-n-octyl phthalate	55	3	*	ND	0.191	*	0.096
	90	2	ND	*	0.023	ND	0.011

TABLE V-7 (Continued)

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
71. dimethyl phthalate	55	3	ND	ND	*	ND	*
	90	2	ND	ND	ND	ND	
73. benzo (a) pyrene	55	3	*	ND	*	ND	*
	90	2	ND	ND	ND	ND	
75. benzo (k)fluoranthene	55	3	ND	ND	*	ND	*
	90	2	ND	ND	ND	ND	
76. chrysene	55	3	*	ND	*	*	*
	90						
78. anthracene (a)	55	3	ND	< 0.014	< 0.017	< 0.010	< 0.014
	90	2	ND	ND	0.011	*	0.006
80. fluorene	55	3	ND	ND	ND	ND	
	90	2	ND	0.221	ND	0.166	0.194
81. phenanthrene (a)	55	3					
	90						
84. pyrene	55	3	ND	ND	ND	*	*
	90	2	ND	ND	ND	ND	
85. tetrachloroethylene	55	3	*	*	ND	ND	*
	90	2	*	ND	0.021	*	0.011
87. trichloroethylene	55	3	ND	*	ND	ND	*
	90	2	ND	ND	ND	ND	
90. dieldrin				ND	**	**	**
91. chlordane	55	3	**	**	**	**	**
	90	2	ND	ND	**	**	**
92. 4,4'-DDT	55	3	ND	**	**	**	**
	90	2	ND	**	**	**	
93. 4,4'-DDE	55	3	ND	**	**	**	**
	90	2	ND	ND	ND	ND	**
95. alpha-endosulfan	55	3	ND	ND	**	**	**

TABLE V-7 (Continued)

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
96. beta-endosulfan	55	3	ND	ND	**	ND	**
97. endosulfan sulfate	55	3	ND	ND	**	**	**
98. endrin	55	3	ND	ND	**	ND	**
	90	2		ND	ND	**	**
99. endrin aldehyde	55	3	**	**	ND	**	**
	90	2					
100. heptachlor	55	3	**	**	ND	**	**
	90	2	ND	**	**	**	**
101. heptachlor epoxide	55	3	**	**	**	**	**
	90	2	ND	**	ND	**	**
102. alpha-BHC	55	3	**	ND	ND	**	**
103. beta-BHC	55	3	**	**	ND	**	**
	90	2	ND	**	**	**	**
104. gama-BHC	55	3	ND	**	ND	**	**
106. PCB-1242 (b)							
107. PCB-1254 (b)	55	3	**	**	**	**	**
	90	2		**	**	**	**
108. PCB-1221 (b)							
110. PCB-1248 (c)	55	3	**	**	**	**	**
	90	2		**	**	**	**
1.1. PCB-1260 (c)							
112. PCB-1016 (c)							
114. antimony	55	3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	90	2	< 0.1	< 0.1	0.6	< 0.1	< 0.2
115. arsenic	55	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	90	2	0.01	0.03	0.03	0.02	0.03
117. beryllium	55	3	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	90	2	< 0.001	0.005	< 0.001	< 0.001	0.002

TABLE V-7 (Continued)

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted) Day 1	Day 2	Day 3	Average
118. cadmium	55	3	< 0.002	< 0.02	< 0.002	< 0.002	< 0.002
	90	2	< 0.002	< 0.002	0.02	0.01	0.010
119. chromium	55	3	< 0.005	0.02	0.01	0.01	0.013
	90	2	< 0.005	< 0.005	0.02	0.02	0.013
120. copper	55	3	0.06	0.02	0.01	0.02	0.017
	90	2	0.02	5	9	8	7
121. cyanide	55	3		0.002	0.003	0.002	0.002
	90	2		0.002	< 0.001	< 0.001	0.001
122. lead	55	3	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
	90	2	0.02	8	2	6	5
123. mercury	55	3	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
	90	2	0.0001	0.0001	0.0001	0.0001	0.0001
124. nickel	55	3	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	90	2	< 0.005	< 0.005	< 0.0005	< 0.0005	< 0.005
125. selenium	55	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
126. silver	55	3	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
127. thallium	55	3	< 0.1	< 0.1	< 0.1	0.2	0.07
	90	2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
128. zinc	55	3	0.060	< 0.060	< 0.060	< 0.060	< 0.060
	90	2	< 0.060	2	2	2	2
Nonconventionals							
chemical oxygen demand (COD)	55	3		14	8	12	11.33
	90	2	< 5	53	50	43	48.67
total organic carbon (TOC)	55	3		1	5	7	4.333
	90	2	3	9	9	7	8.33
phenols (total; by 4-AAP method)	55	3		0.016	0.009	0.013	0.013
	90	2		0.013	0.011	0.011	0.012

TABLE V-7 (Continued)

PRIMARY ELECTROLYTIC COPPER REFINING SAMPLING DATA
TREATED WASTEWATER

Pollutants	Stream Code	Sample Type	Source	Concentrations (mg/l, Except as Noted)			
				Day 1	Day 2	Day 3	Average
Conventionals							
oil and grease	55	1		9	8	2	6
	90	2		11	12	3	8.7
total suspended solids (TSS)	55	3		7	5	6	6
	90	2	1	302	7	57	122
pH (standard units)	55	1		10.2	10.2		
	90	1		10.6	11.3	9.3	

(a), (b), and (c) reported together

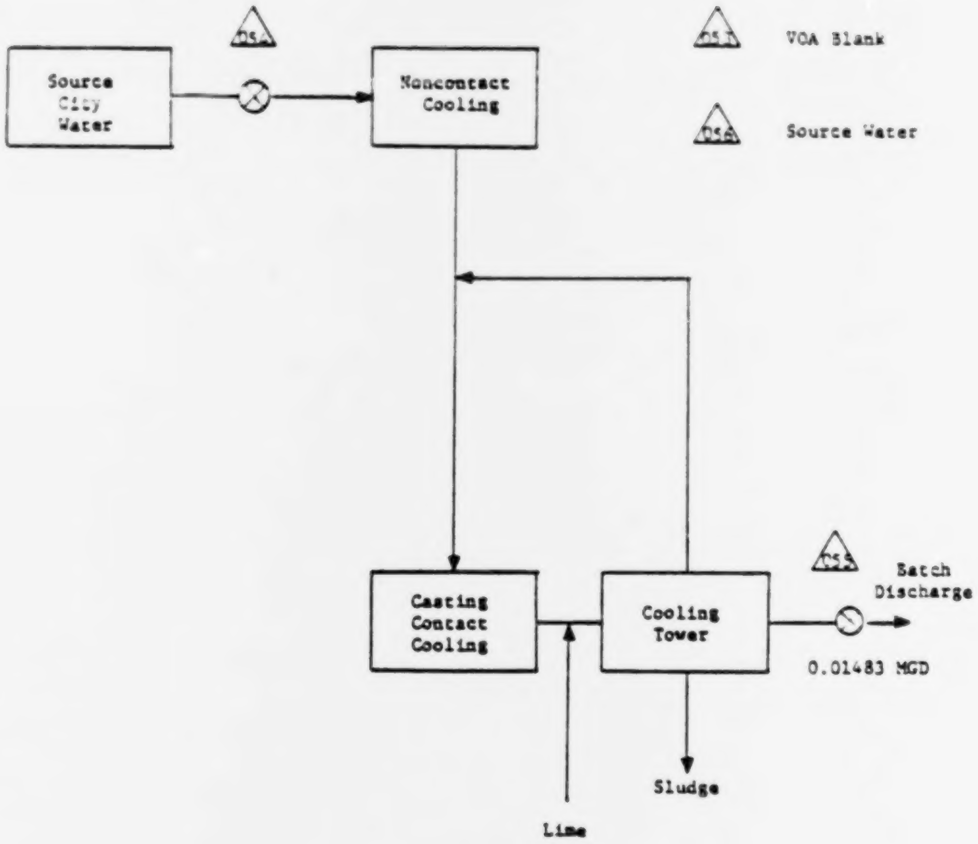
054
Source City Water
Noncontact Cooling
053
VOA Blank
054
Source Water
Casting Contact Cooling
Cooling Tower
055
Batch Discharge
0.01483 MGD
Sludge
Lime

FIGURE V-1
SAMPLING SITES AT PRIMARY COPPER REFINER PLANT A

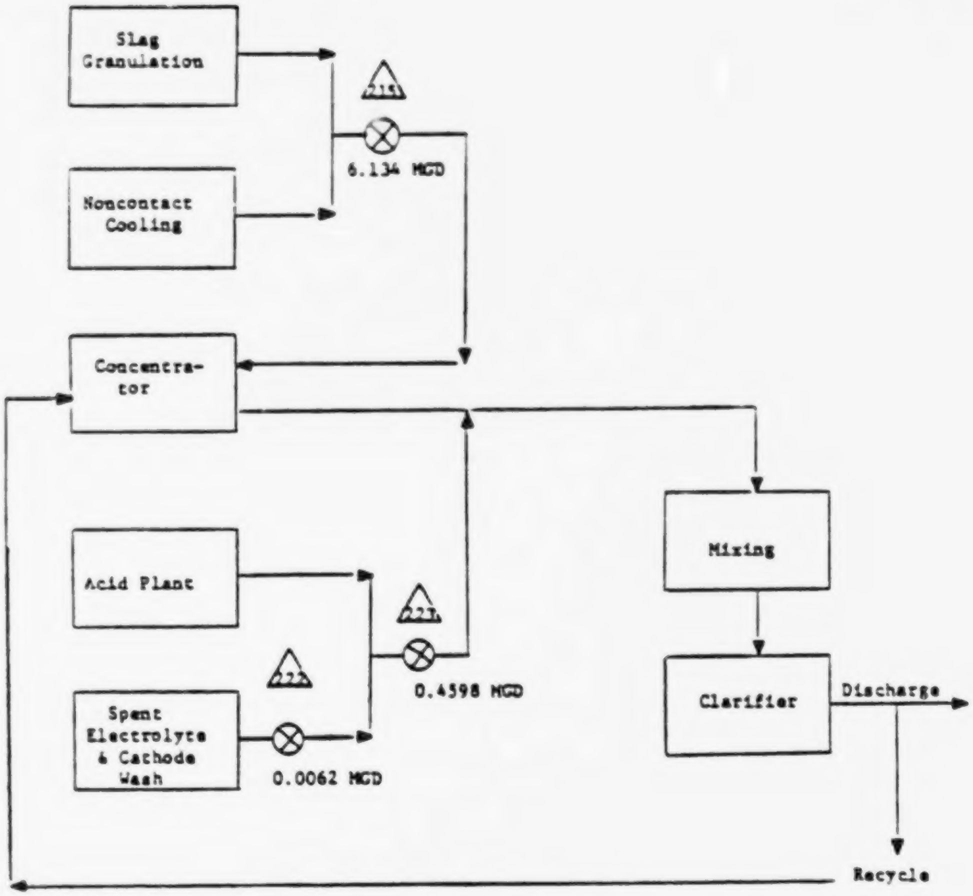
Slag Granulation
Noncontact Cooling
215
6.134 MGD
Concentrator
Acid Plant
223
0.4598 MGD
222
Spent Electrolyte & Cathode Wash
0.0062 MGD
Mixing
Clarifier
Discharge
Recycle

FIGURE V-2
SAMPLING SITES AT PRIMARY COPPER REFINER PLANT C

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

This section examines chemical analysis data presented in Section V from primary electrolytic copper refining plant sampling visits and discusses the selection or exclusion of pollutants for potential limitation in this subcategory.

Each pollutant selected for potential limitation is discussed in Section VI of Vol. 1. That discussion provides information concerning the origin of each pollutant (i.e., whether it is a naturally occurring substance, processed metal, or a manufactured compound), general physical properties and the form of the pollutant, toxic effects of the pollutant in humans and other animals, and behavior of the pollutant in POTW at the concentrations expected in industrial discharges.

The discussion that follows describes the analysis that was performed to select or exclude pollutants for consideration for limitations and standards. Pollutants are considered for limitations and standards if they are present in concentrations treatable by the technologies considered in this analysis. The treatable concentrations used for the toxic metals were the long-term performance values achievable by lime precipitation, sedimentation, and filtration. The treatable concentrations used for the toxic organics were the long-term performance values achievable by carbon adsorption (see Section VII of Vol. 1 -- Combined Metals Data Base).

After the February 1983 proposal, the Agency re-evaluated the treatment performance of activated carbon adsorption to control toxic organic pollutants. The treatment performance for the acid extractable, base-neutral extractable, and volatile organic pollutants has been set equal to the analytical quantification limit of 0.010 mg/l. The analytical quantification limit for pesticides and total phenols (by 4-AAP method) is 0.005 mg/l, which is below the 0.010 mg/l accepted for the other toxic organics. However, to be consistent, the treatment performance of 0.010 mg/l is used for pesticides and total phenols. The 0.010 mg/l concentration is achievable, assuming enough carbon is used in the column and a suitable contact time is allowed. The frequency of occurrence for 36 of the toxic pollutants has been re-determined based on the revised treatment performance value. However, no toxic organic pollutants have been selected for consideration for limitation. The pollutants selected are identical to those selected at proposal, for the reasons discussed below.

CONVENTIONAL AND NONCONVENTIONAL POLLUTANT PARAMETER

This study examined samples from the primary electrolytic copper refining subcategory for three conventional pollutant parameters

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(oil and grease, total suspended solids, and pH) and three nonconventional pollutant parameters (chemical oxygen demand, total organic carbon, and total phenols).

CONVENTIONAL AND NONCONVENTIONAL POLLUTANT PARAMETERS SELECTED

No nonconventional pollutants were selected for limitation in this subcategory. For conventional pollutants, total suspended solids (TSS) and pH were the parameters selected. Total suspended solids concentrations were found to be 18 and 1,140 mg/l from the two samples considered for pollutant selection. These two samples are above the treatable concentration attainable by available specific treatment processes. Furthermore, most of the specific methods for removing toxic metals do so by precipitation, and the resulting toxic metals precipitates should not be discharged. Meeting a limitation on TSS also aids in removal of precipitated toxic metals. For these reasons, total suspended solids is considered for specific limitation in this subcategory.

The pH values obtained from the two samples considered were 1.2 and 7.6. Effective removal of toxic metals by chemical precipitation requires careful control of pH. Therefore, pH is considered for specific limitation in this subcategory.

TOXIC POLLUTANTS

The frequency of occurrence of the toxic pollutants in the wastewater samples taken is presented in Table VI-1 (page 1158). These data provide the basis for the categorization of specific pollutants, as discussed in the following sections. Table VI-1 is based on raw wastewater data from streams 216 and 222 (see Section V). Treatment plant sampling data were not used for the frequency count, although stream 55, containing treated wastewater, was used for toxic organic pollutant selection. During the field sampling program, only stream 55 was tested for toxic organics. The Agency believes, due to raw materials and processing agents, there are no treatable concentrations of toxic organics in wastewaters from electrolytic copper refineries. The waste stream on which the organic analysis was performed was pretreated with chemical precipitation and sedimentation methods. This method of treatment is designed for dissolved metals removal and is expected to have very little effect on the concentration of toxic organics in the wastewater.

TOXIC POLLUTANTS NEVER DETECTED

The toxic pollutants listed in Table VI-2 (page 1159) below were not detected in any raw wastewater samples from this subcategory. Therefore, they are not selected for consideration in establishing limitations.

TOXIC POLLUTANTS NEVER FOUND ABOVE THEIR ANALYTICAL QUANTIFICATION LIMIT

The toxic pollutants listed in Table VI-3 (page 1161) were never found above their analytical quantification concentration in any wastewater samples from this subcategory; therefore, they are not selected for consideration in establishing limitations.

TOXIC POLLUTANTS DETECTED BUT PRESENT SOLELY AS A RESULT OF ITS PRESENCE IN THE INTAKE WATERS

Listed below are those pollutants that were detected above quantification limit but were also detected in the source water or a blank and are therefore not selected for regulation:

23. chloroform (trichloromethane)
66. bis(2-ethylhexyl) phthalate
67. butyl benzyl phthalate
68. di-n-butyl phthalate
69. di-n-octyl phthalate

TOXIC POLLUTANTS PRESENT BELOW CONCENTRATIONS ACHIEVABLE BY TREATMENT

The pollutants listed below are not selected for consideration in establishing limitations because they were not found in any wastewater samples from this subcategory above concentrations considered achievable by existing or available treatment technologies. These pollutants are discussed individually following the list.

114. antimony
125. selenium

Antimony was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of antimony in the sample was 0.400 mg/l. This value is below the 0.47 mg/l concentration considered attainable by identified treatment technology. Therefore, because antimony was not detected above concentrations considered attainable by identified treatment technology, it is eliminated from further consideration for limitation.

Selenium was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of selenium in the sample was 0.015 mg/l. This value is below the 0.20 mg/l concentration considered attainable by identified treatment technology. Therefore, because selenium was not detected above concentrations considered attainable by identified treatment technology, it is eliminated from further consideration for limitation.

TOXIC POLLUTANTS SELECTED FOR CONSIDERATION FOR ESTABLISHING LIMITATIONS AND STANDARDS

The toxic pollutants listed below are selected for further consideration for establishing limitations and standards for this subcategory. The toxic pollutants selected are each discussed following the list:

115. arsenic
119. chromium
120. copper
122. lead
124. nickel
126. silver
128. zinc

Arsenic was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of arsenic in the sample was 1.20 mg/l. This value is above the 0.34 mg/l concentration considered attainable by identified treatment technology. Therefore, arsenic is selected for further consideration for limitation.

Chromium was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of chromium in the sample was 0.076 mg/l. This value is above the 0.070 mg/l concentration considered attainable by identified treatment technology. Therefore, chromium is selected for further consideration for limitation.

Copper was detected above its analytical quantification limit in two of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of copper in the samples was 3.9 mg/l and 1.55 mg/l. This value is above the 0.39 mg/l concentration considered attainable by identified treatment technology. Therefore, copper is selected for further consideration for limitation.

Lead was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of lead in the sample was 1.4 mg/l. This value is above the 0.08 mg/l concentration considered attainable by identified treatment technology. Therefore, lead is selected for further consideration for limitation.

Nickel was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of nickel in the sample was 4,200 mg/l. This value is above the 0.22 mg/l concentration considered attainable by identified treatment technology. Therefore, nickel is selected for further consideration for limitation.

Silver was detected above its analytical quantification limit in one of the two raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of silver in the sample was 0.130 mg/l. This value is above the 0.070 mg/l concentration considered attainable by identified treatment technology. Therefore, silver is selected for further consideration for limitation.

Zinc was detected above its analytical quantification limit in both of the raw wastewater samples taken from the primary electrolytic copper refining subcategory. The concentration of zinc in the samples was 31.5 mg/l and 0.052 mg/l. A value of 31.5 mg/l is well above the 0.23 mg/l concentration considered attainable by identified treatment technology. Therefore, zinc is selected for further consideration for limitation.

TABLE VI-1

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
PRIMARY ELECTROLYTIC COPPER REFINING
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentrations (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	ND	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
114. antimony	0.100	0.47	2	2	1		1	
115. arsenic	0.010	0.34	2	2	1			1
116. asbestos	10 MFL	10 MFL	1	1	1			
117. beryllium	0.010	0.20	2	2	2			
118. cadmium	0.002	0.49	2	2	2			
119. chromium	0.005	0.07	2	2	1			1
120. copper	0.009	0.39	2	2				2
121. cyanide	0.02(c)	0.047	1	1	1			
122. lead	0.020	0.08	2	2	1			1
123. mercury	0.0001	0.036	2	2	2			
124. nickel	0.005	0.22	2	2	1			1
125. selenium	0.01	0.20	2	2	1		1	
126. silver	0.02	0.07	2	2	1			1
127. thallium	0.100	0.34	2	2	2			
128. zinc	0.050	0.23	2	2			1	1

(a) Analytical quantification concentration was reported with the data (see Section V).

(b) Treatable concentrations are based on performance of lime precipitation, sedimentation, and filtration.

(c) Analyzed quantification concentration for EPA Method 335.2, Total Cyanide Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979.

TABLE VI-2

TOXIC POLLUTANTS NEVER DETECTED

2. acrolein
3. acrylonitrile
5. benzidene
6. carbon tetrachloride (tetrachloromethane)
7. chlorobenzene
8. 1,2,4-trichlorobenzene
9. hexachlorobenzene
10. 1,2-dichloroethane
12. hexachloroethane
13. 1,1-dichloroethane
14. 1,1,2-trichloroethane
16. chloroethane
17. DELETED
18. bis(2-chloroethyl) ether
19. 2-chloroethyl vinyl ether (mixed)
20. 2-chloronaphthalene
21. 2,4,6-trichlorophenol
22. parachlorometa cresol
24. 2-chlorophenol
25. 1,2-dichlorobenzene
26. 1,3-dichlorobenzene
27. 1,4-dichlorobenzene
28. 3,3'-dichlorobenzidine
31. 2,4-dichlorophenol
32. 1,2-dichloropropane
33. 1,2-dichloropropylene (1,3-dichloropropene)
34. 2,4-dimethylphenol
35. 2,4-dinitrotoluene
36. 2,6-dinitrotoluene
37. 1,2-diphenylhydrazine
38. ethylbenzene
40. 4-chlorophenyl phenyl ether
41. 4-bromophenyl phenyl ether
42. bis(2-chloroisopropyl) ether
43. bis(2-choroethoxy) methane
44. methylene chloride (dichloromethane)
45. methyl chloride (chloromethane)
46. methyl bromide (bromomethane)
47. bromoform (tribromomethane)
48. dichlorobromomethane
49. DELETED
50. DELETED
51. chlorodibromomethane
52. hexachlorobutadiene
53. hexachlorocyclopentadiene
54. isophorone
56. nitrobenzene
57. 2-nitrophenol
58. 4-nitrophenol
59. 2,4-dinitrophenol
60. 4,6-dinitro-o-cresol

TABLE VI-2 (Continued)

TOXIC POLLUTANTS NEVER DETECTED

61. N-nitrosodimethylamine
62. N-nitrosodiphenylamine
63. N-nitrosodi-n-propylamine
64. pentachlorophenol
65. phenol
70. diethyl phthalate
72. benzo(a)anthracene (1,2-benzanthracene)
74. 3,4-benzofluoranthene
77. acenaphthylene
79. benzo(ghi)perylene (1,11-benzoperylene)
80. fluorene
82. dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)
83. indeno(1,2,3-cd)pyrene (w,e,-o-phenylenepyrene)
86. toluene
88. vinyl chloride (chlorethylene)
89. aldrin
90. dieldrin
94. 4,4'DDD (p,p'TDE)
105. delta-BHC
113. toxaphene
116. asbestos (Fibrous)
117. beryllium
118. cadmium
121. cyanide (Total)
123. mercury
127. thallium
129. 2,3,7,8-tetra chlorodibenzo-p-dioxin (TCDD)

TABLE VI-3

TOXIC POLLUTANTS NEVER FOUND ABOVE THEIR ANALYTICAL QUANTIFICATION LIMIT

1. acenaphthene
4. benzene
11. 1,1,1-trichlorethane
15. 1,1,2,2-tetrachloroethane
29. 1,1-dichloroethylene
30. 1,2-_trans_-dichloroethylene
39. fluoranthene
55. naphthalene
71. dimethyl phthalate
73. benzo(a)pyrene (3,4-benzopyrene)
75. benzo(k)fluoranthane (11,12-benzofluoranthene)
76. chrysene
78. anthracene (a)
81. phenanthrene (a)
84. pyrene
85. tetrachloroethylene
87. trichloroethylene
91. chlordane (technical mixture and metabolites)
92. 4,4'-DDT
93. 4,4'-DDE (p,p'DDX)
95. a-endosulfan-Alpha
96. b-endosulfan-Beta
97. endosulfan sulfate
98. endrin
99. endrin aldehyde
100. heptachlor
101. heptachlor epoxide
102. a-BHC-Alpha
103. b-BHC-Beta
104. r-BHC (lindane)-Gamma
106. PCB-1242 (Arochlor 1242) (b)
107. PCB-1254 (Arochlor 1254) (b)
108. PCB-1221 (Arochlor 1221) (b)
109. PCB-1232 (Arochlor 1232) (c)
110. PCB-1248 (c)
111. PCB-1260 (Arochlor 1260) (c)
112. PCB-1016 (Arochlor 1016) (c)

(a), (b), (c) Reported together, as a combined value.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

The preceding sections of this supplement discussed the waste water sources, flows, and characteristics of the wastewaters from primary electrolytic copper refining plants. This section summarizes the description of these wastewaters and indicates the level of treatment which is currently practiced by the primary electrolytic copper refining industry for each waste stream.

TECHNICAL BASIS OF BPT

As mentioned in Section III, EPA promulgated BPT effluent limitations guidelines for the primary electrolytic copper refining subcategory on July 2, 1980. The BPT regulations established by EPA limit the discharge of copper, cadmium, lead, zinc, and TSS, and require the control of pH. The best practicable control technology identified is the treatment of wastewater by lime and settle technology. To obtain the values required at BPT, the agency acknowledges that in some cases it may be necessary to use chemical flocculants to enhance settling.

CURRENT CONTROL AND TREATMENT PRACTICES

This section presents a summary of the control and treatment technologies that are currently applied to each of the sources generating wastewater in this subcategory. As discussed in Section V, wastewater associated with the primary copper electrolytic refining subcategory is characterized by the presence of the toxic metal pollutants and suspended solids. (The raw (untreated) wastewater data for specific sources as well as combined waste streams is presented in Section V.) Generally, these pollutants are present in each of the waste streams at treatable concentrations, so these waste streams are commonly combined for treatment to reduce the concentrations of these pollutants. Construction of one wastewater treatment system for combined treatment allows plants to take advantage of economies of scale and, in some instances, to combine streams of differing alkalinity to reduce treatment chemical requirements. Ten plants in this subcategory currently have combined wastewater treatment systems, five have lime precipitation and sedimentation, and no plants have lime precipitation, sedimentation, and filtration. After proposal, three options were selected for consideration for BAT, BDT, and pretreatment in this subcategory, based on combined treatment of these compatible waste streams.

ELECTROLYTIC REFINING

Copper anodes obtained from smelters are inserted in an electrolytic bath consisting of sulfuric acid and copper sulfate. As copper ions migrate from the anode to the cathode, impurities contained within the anode are released. Several of these

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impurities are soluble in the electrolyte, while others, such as precious metals, are not, and they settle to the bottom of the cells. A bleed stream is continuously removed from the electrolytic tank house to control the levels of soluble impurities and the concentration of copper sulfate in the electrolyte. The bleed stream is electrowinned to remove copper present as copper sulfate, and then partially evaporated to initiate the precipitation of nickel sulfate. At most refineries the stream is returned to the tank house as make up acid. One plant, however, reported discharging this waste stream after pH adjustment and sedimentation. Two refineries located in areas of net evaporation reported partial recycle and evaporation of spent electrolyte. Two facilities reported the sale of spent electrolyte to copper sulfate manufacturers. One plant reported disposing of its spent electrolyte in a deep well, and three facilities did not provide information on treatment practices. The remaining six electrolytic refiners reported a 100 percent recycle of spent electrolyte.

Spent electrolyte after electrowinning and nickel sulfate removal is characterized by a low pH (2.5) with dissolved treatable toxic metals. This waste stream is treatable through pH adjustment to precipitate the dissolved metals and settling to remove the precipitate. A better method, as demonstrated in the subcategory, is complete recycle after electrowinning and nickel sulfate removal to eliminate the discharge of all toxic pollutants.

ANODE AND CATHODE RINSE WATER

Anodes are removed from the electrolytic cells in monthly cycles and often rinsed before being returned to a casting furnace. There were six plants who reported washing anode butts upon removal from the cells, five of which reported a zero discharge or 100 percent recycle of this wastewater. Generally the washing is done above the cells so that all wastewater is captured in the cell and not discharged. One facility reported discharging a blowdown from this waste stream as it was recycled. This facility also indicated that the blowdown was not treated before discharge.

As with spent electrolyte, anode and cathode rinse water is characterized by a low pH with dissolved toxic metals. Accordingly, this waste stream is treatable through pH adjustment to precipitate the dissolved metals and settling to remove the precipitate. Industry has demonstrated, however, that this waste stream can be eliminated if anodes and cathodes are rinsed above the electrolytic cells.

CASTING

Blister copper and anode copper are cast into usable shapes for further processing. Wastewater from this operation is due to contact cooling and furnace scrubber liquor. From dcp responses it was determined that two of four plants discharging casting contact cooling water recycle greater than 90 percent of the water used. Before discharge, two plants treat the cooling water with lime and settle technology, one plant passes its water through settling ponds before discharge, and the other plant discharges a blow down from its cooling tower without treatment. To achieve zero discharge, a variety of methods are used, including chemical precipitation and sedimentation followed by 100 percent recycle, deep well injection, cooling towers, solar evaporation, and 100 percent reuse in other plant processes.

Both casting contact cooling and casting scrubber liquor will exhibit similar wastewater characteristics, treatable concentrations of dissolved metals and suspended solids. Wastewater from these two sources is best treated with lime and settle technology. Further reduction of pollutant discharge can be accomplished through cooling towers and recycle.

CASTING SCRUBBER LIQUOR

Control of particulate matter from casting furnaces is accomplished with a wet system at one plant with ultimate disposal of this wastewater through deep well injection. The remaining refineries reported no control of emissions from casting furnaces.

BY-PRODUCT RECOVERY

Many of the impurities present in anode copper have economic value and may be recovered as a by-product of electrolytic copper refining. From the dcp responses, it was determined that three electrolytic refiners recover precious metals on site as by-products. Of these three facilities, one plant reported discharging wastewater from the processing of anode slimes and wastewater from a fusion kiln SO_2 scrubber; while one reported discharging wastewater through deep well injection, and one reported 100 percent recycle. The plant practicing 100 percent recycle treats the wastewater by iron cementation and neutralization with caustic before reusing the water.

The principal source of wastewater from by-product recovery is due to leaching and precipitation throughout the by-product recovery process to remove impurities. Many of the spent solutions are acidic and could be treated through pH adjustment to initiate precipitation followed by sedimentation. EPA believes, however, that these wastewaters can be recycled or reused in other processes. This is demonstrated by one facility located in an area of net precipitation.

CONTROL AND TREATMENT OPTIONS

Based on an examination of the wastewater sampling data, three control and treatment technologies that effectively control the pollutants found in primary electrolytic copper refining waste waters were selected for evaluation. Other treatment technologies considered for the category included activated alumina adsorption (Option D) and activated carbon adsorption (Option E). However, these technologies were not selected for evaluation in this subcategory because they are not applicable to primary electrolytic copper refining. Although arsenic was found in process wastewaters at treatable concentrations, activated alumina technology (Option D) is not demonstrated in the nonferrous metals manufacturing category, nor is it clearly transferable. No toxic organic pollutants were found in process waste waters above their treatable concentrations. Also, organic pollutants are not characteristics of the raw materials and processing agents used in this subcategory. Therefore, activated carbon is not considered necessary. The options selected for evaluation are discussed below.

OPTION A

Option A for the primary electrolytic copper refining subcategory is equivalent to BPT. The BPT model end-of-pipe treatment consists of chemical precipitation and sedimentation (lime and settle) technology. Chemical precipitation and sedimentation removes metals and suspended solids from the casting contact cooling water by the addition of lime followed by sedimentation.

OPTION B

Option B for the primary electrolytic copper refining subcategory requires control and treatment technologies to reduce the discharge of wastewater volume and pollutant mass. Water recycle and reuse are the principal control mechanisms for flow reduction.

The Option B treatment model is based on the same chemical precipitation and sedimentation technology as BPT (Option A), but it allows a discharge from casting contact cooling only. Recycle and reuse are also required for casting contact cooling water to control solids. A 100 percent recycle or reuse are required for spent electrolyte and anode and cathode rinse water. Chemical precipitation is used to remove metals by the addition of lime followed by settling. Suspended solids are also removed from the process.

OPTION C

The Option C treatment scheme builds on Option B (treatment of chemical precipitation, sedimentation, and in-process flow reduction) with the addition of preliminary treatment consisting of sulfide precipitation, pressure filtration, and multimedia filtration end-of-pipe treatment. Sulfide precipitation is used to further reduce the concentration of dissolved metals at one primary copper refiner operating a metallurgical acid plant. Multimedia filtration is used to remove suspended solids, including precipitates of metals beyond the concentration attainable by gravity sedimentation. The filter suggested is of the gravity, mixed media type, although other forms of filters such as rapid sand filters or pressure filters would perform satisfactorily. The addition of filters also provides consistent removal during periods of time in which there are rapid increases in flows or loadings of pollutants to the treatment system.

TREATMENT TECHNOLOGIES REJECTED AT PROPOSAL

Other treatment technologies included activated alumina adsorption (Option D), activated carbon adsorption (Option E), and reverse osmosis (Option F). These technologies were not considered because they are not applicable to the primary electrolytic copper refining subcategory. Although arsenic was found in process wastewaters at treatable concentrations, activated alumina technology (Option D) is not demonstrated in the nonferrous metals manufacturing category, nor is it clearly transferable. Activated carbon adsorption technology (Option E) was not considered because treatable concentrations of toxic organic pollutants were not detected in wastewater from primary copper electrolytic refiners. Also, organic pollutants are not characteristic of the raw materials and processing agents used in this subcategory. Therefore, activated carbon adsorption is not applicable.

Option F for the primary copper refining subcategory consisted of reverse osmosis and evaporation technology added at the end of the lime precipitation, sedimentation, in-process flow reduction, and multimedia filtration considered for Option C. Option F was used for complete recycle of the treated water by controlling the concentration of dissolved solids. Multiple-effect evaporation is used to dewater the brines rejected from reverse osmosis. Reverse osmosis, however, was rejected because it was not demonstrated in the nonferrous metals manufacturing category, nor is it clearly transferable.

SECTION VIII

COSTS, ENERGY, AND NONWATER QUALITY ASPECTS

This section describes the method used to develop the costs associated with the control and treatment technologies discussed in Section VII for wastewaters from primary electrolytic copper refining plants. The energy requirements of the considered options as well as solid waste and air pollution aspects are also discussed in this section.

Cost estimates, based on the preliminary and end-of-pipe treatment of casting contact cooling and spent electrolyte water, are presented in this section for the primary electrolytic copper refining subcategory.

In Section VI of this supplement, several pollutants and pollutant parameters are selected for limitation for the primary electrolytic copper refining subcategory. These pollutants or pollutant parameters include copper, lead, nickel, total suspended solids, and pH. Metals are most economically removed by chemical precipitation, sedimentation, and filtration. The recycle of casting contact cooling water through cooling towers may also be added as a preliminary flow reduction measure which decreases the discharge flow from casting and results in the concentration of pollutants in the effluent stream. Treatment of a more concentrated effluent allows achievement of a greater net pollutant removal and introduces the possible economic cost-effectiveness associated with treating a lower volume of wastewater. Therefore, the basic control and treatment technologies considered for the primary electrolytic copper refining subcategory are cooling towers, chemical precipitation and sedimentation (lime and settle and filtration), with preliminary treatment for arsenic with sulfide precipitation and pressure filtration where appropriate.

TREATMENT OPTIONS CONSIDERED

As discussed in Section VII of this supplement, three control and treatment options are considered for treating wastewater from the primary electrolytic copper refining subcategory. The control and treatment options are described below and schematically presented in Figures X-1 through X-3 (pages 1189 - 1193).

OPTION A

Casting contact cooling wastewater and spent electrolyte are treated by chemical precipitation and sedimentation. This option represents no additional costs since the promulgated 1980 BPT is based on lime precipitation and sedimentation.

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OPTION B

The casting contact cooling water is recycled through a cooling tower and a blowdown stream, along with spent electrolyte, is treated by chemical precipitation and sedimentation.

OPTION C

The casting contact cooling water is recycled through a cooling tower and a blowdown stream, along with spent electrolyte, and is treated by chemical precipitation, sedimentation, sulfide precipitation (and filtration), and multimedia filtration. The sulfide precipitation is included for one primary copper refiner operating a metallurgical acid plant. The cost of the sulfide precipitation is attributed entirely to the acid plant.

COSTING METHODOLOGY

A detailed discussion of the methodology used to develop the compliance costs is presented in Section VIII of the General Development Document. Plant-by-plant compliance costs have been estimated for the nonferrous metals manufacturing category and are presented in the administrative record supporting this regulation. A comparison of the costs developed for proposal and the revised costs for the final regulation are presented in Table VIII-1 (page 1173) for the direct discharges.

Each of the major assumptions used to develop compliance costs is presented in Section VIII of the General Development Document. Each subcategory contains a unique set of waste streams requiring certain subcategory-specific assumptions to develop compliance costs. Five major assumptions are discussed briefly below.

(1) No discharge of process wastewater from the anode and cathode rinse operation is accomplished via in-plant process modifications. As such, no compliance costs are attributable to this regulation.

(2) Because the compliance costs need only represent incremental costs that primary copper refineries may be expected to incur in complying with this regulation, operation and maintenance costs for in-place treatment used to comply with the previously promulgated BPT regulation for this subcategory are not included in a plant's total cost of compliance for this regulation.

(3) Capital and annual costs for the plant discharging wastewater in both the primary copper and metallurgical acid plant subcategories are attributed to each subcategory on a flow-weighted basis.

(4) No cost is included for direct discharges to comply with elimination of net precipitation allowances for primary copper plants.

(5) Recycle of casting contact cooling water is based on recycle through cooling towers. Annual costs associated with maintenance and chemicals to prevent biological growth, corrosion, and scale formation are included in the estimated compliance costs. If a plant currently recycles casting contact cooling water, capital costs of the recycle equipment (cooling tower, pumps, and piping) were not included in the compliance costs.

NONWATER QUALITY ASPECTS

Nonwater quality impacts specific to primary electrolytic copper refining, including energy requirements, solid waste and air pollution are discussed below.

ENERGY REQUIREMENTS

The methodology used for determining the energy requirements for the various options is discussed in Section VIII of the General Development Document. Energy requirements are estimated at 0.14 MW-hr/yr and 0.17 MW-hr/yr for Options B and C, respectively. No additional energy is required for Option A as a result of this regulation since BPT is in place. Option C represents roughly five percent of a typical plant's electrical usage. It is therefore concluded that the energy requirements of the treatment options considered will have no significant impact on total plant energy consumption.

SOLID WASTE

Sludges associated with the primary electrolytic copper refining subcategory will necessarily contain additional quantities (and concentrations) of toxic metal pollutants. Wastes generated by primary smelters and refiners are currently exempt from regulation by Act of Congress (Resource Conservation and Recovery Act (RCRA), Section 3001(b). Consequently, sludges generated from treating primary industries' wastewater are not presently subject to regulation as hazardous wastes.

The technology basis for one plant in the primary copper electrolytic refining subcategory includes separate sulfide precipitation for the control of arsenic. In developing compliance costs for this plant, sulfide precipitation was used as a preliminary treatment to lime, settle, and multimedia filtration treatment. Precipitants generated during sulfide precipitation are removed in a pressure filter and backwashed to lime and settle. The Agency believes sludge generated through sulfide precipitation will be classified as hazardous under RCRA. The costs of hazardous waste disposal were considered in the economic analysis for the one copper plant (even though the waste is now exempt from RCRA regulation) and they were determined to be economically achievable. Sludges generated by the other primary copper direct discharges are not expected to be hazardous if a small (5-10%) excess of lime is added during treatment. Multimedia filtration will not generate any significant amount of sludge over that resulting from lime precipitation and sulfide precipitation.

Although it is the Agency's view that lime sludges generated as a result of these guidelines are not expected to be hazardous (except for the one plant), generators of these wastes must test the waste to determine if the wastes meet any of the characteristics of hazardous waste (see 40 CFR 262.11).

If these wastes should be identified or are listed as hazardous, they will come within the scope of RCRA's "cradle to grave" hazardous waste management program, requiring regulation from the point of generation to point of final disposition. EPA's generator standards would require generators of hazardous nonferrous metals manufacturing wastes to meet containerization, labeling, recordkeeping, and reporting requirements; if plants dispose of hazardous wastes off-site, they would have to prepare a manifest which would track the movement of the wastes from the generator's premises to a permitted off-site treatment, storage, or disposal facility. See 40 CFR 262.20 45 FR 33142 (May 19, 1980), as amended at 45 FR 86973 (December 31, 1980). The transporter regulations require transporters of hazardous wastes to comply with the manifest system to assure that the wastes are delivered to a permitted facility. See 40 CFR 263.20 45 FR 33151 (May 19, 1980), as amended at 45 FR 86973 (December 31, 1980). Finally, RCRA regulations establish standards for hazardous waste treatment, storage, and disposal facilities allowed to receive such wastes. See 40 CFR Part 464 46 FR 2802 (January 12, 1981), 47 FR 32274 (July 26, 1982). Must be disposed of in compliance with the Subtitle D open dumping standards, implementing 4004 of RCRA. See 44 FR 53438 (September 13, 1979). The Agency has calculated as part of the costs for wastewater treatment the cost of hauling and disposing of these wastes.

AIR POLLUTION

There is no reason to believe that any substantial air pollution problems will result from implementation of chemical precipitation, sedimentation, multimedia filtration and reverse osmosis. These technologies transfer pollutants to solid waste and do not involve air stripping or any other physical process likely to transfer pollutants to air. Minor amounts of sulfur may be emitted during sulfide precipitation, and water vapor containing some particulate matter will be released in the drift from the cooling tower systems which are used as the basis for flow reduction in the primary electrolytic copper refining subcategory. However, the Agency does not consider this impact to be significant.

TABLE VIII-1

COST OF COMPLIANCE FOR THE PRIMARY COPPER SUBCATEGORY
DIRECT DISCHARGERS
(March, 1982 Dollars)

Option	Proposal Costs		Promulgation Costs	
	Capital	Annual	Capital	Annual
B	2,120,000	1,549,000	197,000	133,000
C	3,153,000	1,876,000	266,000	171,000

SECTION IX

BEST PRACTICABLE TECHNOLOGY CURRENTLY AVAILABLE

EPA promulgated BPT effluent limitations for the primary copper smelting and electrolytic refining subcategories on July 2, 1980, as Subpart D and Subpart E of 40 CFR Part 421. EPA is not making any modifications to these limitations. Subpart E applies to primary electrolytic copper refining and by-product recovery operations and allows a discharge of process wastewater subject to mass-based limitations.

Pollutants regulated by these limitations are copper, cadmium, lead, zinc, total suspended solids and pH. The effluent limitations established by BPT standards for the primary electrolytic copper refining subcategory are based on chemical precipitation and sedimentation and are as follows:

EFFLUENT LIMITATIONS

Effluent Characteristic	Maximum for Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed
Metric Units - kilograms per 1,000 kg of product English Units - lbs per 1,000 lbs of product		
Total Suspended Solids	0.100	0.050
Copper	0.0017	0.0008
Cadmium	0.0006	0.00003
Lead	0.0006	0.00026
Zinc	0.0012	0.0003
pH	within the range of 6.0 to 9.0	

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SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

These effluent limitations are based on the best control and treatment technology used by a specific point source within the industrial category or subcategory, or by another category where it is readily transferable. Emphasis is placed on additional treatment techniques applied at the end of the treatment systems currently used for BPT, as well as reduction of the amount of water used and discharged, process control, and treatment technology optimization.

The factors considered in assessing best available technology economically achievable (BAT) include the age of equipment and facilities involved, the processes used, process changes, nonwater quality environmental impacts (including energy requirements), and the costs of application of such technology (Section 304 (b) (2) (B) of the Clean Water Act). At a minimum, BAT represents the best available technology economically achievable at plants of various ages, sizes, processes, or other characteristics. Where the Agency has found the existing performance to be uniformly inadequate, BAT may be transferred from a different subcategory or category. BAT may include feasible process changes or internal controls, even when not in common industry practice.

The required assessment of BAT considers costs and economic achievability, but does not require a balancing of costs against effluent reduction benefits (see Weyerhaeuser v. Costle, 590 F.2d. 1011 (D.C. Cir. 1978)). However, in assessing BAT, the Agency has given substantial weight to the economic achievability of the technology.

TECHNICAL APPROACH TO BAT

The Agency reviewed a wide range of technology options and evaluated the available possibilities to ensure that the most effective and beneficial technologies were used as the basis of BAT. To accomplish this, the Agency elected to examine four technology options prior to proposing mass limitations which could be applied to the primary electrolytic copper refining subcategory as BAT options. Three of these technology options were re-evaluated prior to promulgation of mass limitations for the primary copper electrolytic refining subcategory.

In summary, the treatment technologies considered for the primary electrolytic copper refining subcategory are:

Option A (Figure X-1 page 1191) is based on

- o Chemical precipitation and sedimentation

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Option B (Figure X-2 page 1192) is based on

- Chemical precipitation and sedimentation
- Flow reduction

Option C (Figure X-3 page 1193) is based on

- Sulfide precipitation and pressure filtration (at one plant)
- Chemical precipitation and sedimentation
- Flow reduction
- Multimedia filtration

These three technology options considered for BAT are discussed in greater detail below. The first option considered is the same as the BPT treatment and control technology. The remaining options provide additional pollutant removal beyond that achieved by BPT.

OPTION A

Option A for the primary electrolytic copper refining subcategory is chemical precipitation and sedimentation (lime and settle). Chemical precipitation and sedimentation, the technology established as BPT for the primary electrolytic copper refining subcategory, removes metals and suspended solids from the casting contact cooling water and spent electrolyte by the addition of lime followed by sedimentation.

OPTION B

Option B for the primary copper refining subcategory decreases pollutant discharge by building upon the BPT end-of-pipe treatment technology, chemical precipitation and sedimentation (Option A) by including flow reduction measures. Flow reduction measures, including in-process changes, result in the elimination of some wastewater streams and the concentration of pollutants in other effluents as explained in Section VII of Vol. 1. Treatment of a more concentrated effluent allows achievement of a greater net pollutant removal and introduces the possible economic benefits associated with treating a lower volume of wastewater. Methods used in Option B to reduce process wastewater generation or discharge rates include a 100 percent recycle of anode and cathode rinse water and partial recycle of casting contact cooling water.

Recycling of Casting Contact Cooling Water Through Cooling Towers

The cooling and recycle of contact cooling water is practiced by six of the nine plants reporting this wastewater. The function of casting contact cooling water is to quickly remove heat from the newly formed casting product. Therefore, the principal requirements of the water are that it be cool and not contain dissolved solids at a concentration that would cause water marks or other surface imperfections. There is sufficient experience with casting contact cooling wastewater within the nonferrous metals manufacturing category to assure the success of this technology using cooling towers or heat exchangers (refer to Section VII of the General Development Document). Although two plants have reported that they do not discharge any casting contact cooling wastewater, a blowdown or periodic cleaning may be needed to prevent a build-up of dissolved and suspended solids. (EPA has determined that a blowdown of 10 percent of the water applied in a process is adequate).

Recycle of Water Used in Anode and Cathode Rinsing

Total recycle or reuse of anode rinse water is practiced by six of the seven plants generating this wastewater. The amount of recycle used by the single discharging plant was not reported.

The Option B treatment scheme consists of cooling towers for the casting cooling water followed by the treatment scheme of Option A, which consists of chemical precipitation and sedimentation technology (lime and settle).

OPTION C

Option C for the primary electrolytic copper refining subcategory consists of preliminary treatment with sulfide precipitation and pressure filtration and multimedia filtration end-of-pipe technology added to the lime precipitation, sedimentation, and in-process flow reduction considered for Option B. The Option C treatment scheme is presented in Figure X-3 (page 1195). Sulfide precipitation is considered for one primary copper refiner and smelter operating a metallurgical acid plant. Sulfide precipitation followed by pressure filtration will remove toxic metals to levels otherwise achievable by lime and settle treatment. Multimedia filtration is used to remove suspended solids, including precipitates of metals, beyond the concentration attainable by gravity sedimentation. The filter suggested is of the gravity, mixed media type, although other forms of filters, such as rapid sand filters or pressure filters, would perform satisfactorily.

INDUSTRY COST AND POLLUTANT REMOVAL ESTIMATES

As one means of evaluating each technology option, EPA developed estimates of the pollutant removal estimates and the compliance costs associated with each option. The methodologies are described on the following pages.

ESTIMATED POLLUTANT REMOVALS

A complete description of the methodology used to calculate the estimated pollutant reduction achieved by the application of the various treatment options is presented in Section X of the General Development Document. The pollutant removal estimates have been revised from proposal based on comments and on new data; however, the methodology for calculating pollutant removals was not changed. The data used for estimating removals are the same as those used to revised the compliance costs.

Sampling data collected during the field sampling program were used to characterize the major waste streams considered for regulation. At each sampled facility, the sampling data were production normalized for each unit operation (i.e., mass of pollutant generated per mass of product manufactured). This value, referred to as the raw waste, was used to estimate the mass of toxic pollutants generated within the primary electrolytic copper refining subcategory. By multiplying the total subcategory production for a unit operation by the corresponding raw waste value, the mass of pollutant generated for that unit operation was estimated.

The volume of wastewater discharged after the application of each treatment option was estimated for each operation at each plant by comparing the actual discharge to regulatory flow. The smaller of the two values was selected and summed with the other plant flows. The mass of pollutant discharged was then estimated by multiplying the achievable concentration values attainable by the option (mg/l) by the estimated volume of process wastewater discharged by the subcategory. The mass of pollutant removed is the difference between the estimated mass of pollutant generated within the subcategory and the mass of pollutant discharged after application of the treatment option. The pollutant removal estimates for the primary electrolytic copper direct dischargers are presented in Table X-1 (page 1187).

COMPLIANCE COSTS

Compliance costs presented at proposal were estimated using cost curves, relating the total costs associated with installation and operation of wastewater treatment technologies to plant process wastewater discharge. EPA applied these curves on a per plant basis, a plant's costs -- both capital, and operating and maintenance -- being determined by what treatment it has in place and by its individual process wastewater discharge (from dcp). The final step was to annualize the capital costs, and to sum the annualized capital costs, and the operating and maintenance costs, yielding the cost of compliance for the subcategory. Since proposal, the cost estimation methodology has been revised as discussed in Section VIII of this document. A design model and plant specific information were used to size a wastewater treatment system for each discharging facility. After completion of the design, capital and annual costs were estimated for each unit of the wastewater treatment system. Capital costs were developed from vendor quotes and annual costs were developed from literature. Table VIII-1 (page 1173) shows the revised compliance costs of the various options for the primary electrolytic copper refining subcategory.

The compliance costs presented in Section VIII represent the incremental cost of wastewater treatment not already in place. For example, if a plant operates a lime precipitation and sedimentation treatment system of sufficient size, capital costs are not included in the compliance costs estimates since this expenditure has already been incurred by the plant. It is also worth noting that a comparison was made between actual flows and the regulatory flows. The smaller of the two was chosen to use for sizing of the wastewater treatment equipment. The cost of flow reduction was accounted for by developing costs for cooling towers and holding tanks to allow for recycle.

BAT OPTION SELECTION

EPA proposed both Option B and Option C as the basis for alternative BAT effluent limitations for the primary electrolytic copper refining subcategory due to adverse structural economic changes that were not reflected in the Agency's economic analysis. These alternative limitations were based on lime precipitation, sedimentation, and in-process control technologies to reduce the volume of process wastewater discharged for Option B. Lime precipitation, sedimentation, in-process control technologies, and multimedia filtration were proposed for Option C.

As discussed earlier, plant-by-plant compliance costs have been re-evaluated for this subcategory. In addition, the economic analysis, the Agency has determined that Option C, which includes in-process flow reduction, lime precipitation, sedimentation, and multimedia filtration with sulfide precipitation preliminary treatment, is economically achievable. Therefore, the promulgated BAT technology basis for primary copper electrolytic refining is based on Option C technology. Figure X-3 (page 1193) illustrates this treatment scheme.

Filtration is not demonstrated in this subcategory, but it is transferred from the primary aluminum, secondary copper, primary zinc, primary lead, secondary lead, and secondary silver subcategories.

Extensive effluent data submitted to the Agency by an integrated copper refiner and smelter have indicated that the proposed arsenic mass limitations based on lime and settle treatment may not be achievable for this plant. The Agency believes that the larger arsenic values in the plant's ore contribute significant quantities of arsenic to the treatment system. Arsenic concentrations in excess of 100 mg/l are common at this plant, making the combined metals data base inappropriate. The Agency believes that the mass limitations as proposed for the primary electrolytic copper refining subcategory and metallurgical acid plant subcategory are achievable for this plant by adding sulfide precipitation followed by pressure filtration to the model treatment technology. The Agency thus has determined that the combination of sulfide precipitation preliminary treatment, and lime precipitation, sedimentation, and multimedia filtration end-of-pipe technology will achieve the mass limitations promulgated and has included this technology in its compliance cost estimates for this one plant. However, the costs associated with sulfide precipitation on the total process flow were attributed entirely to the metallurgical acid plants subcategory because the refinery wastewater contributes only a small fraction of the combined discharge.

EPA estimates that the promulgated BAT will remove 48,730 kg/yr of toxic metals over raw discharge estimates. The final BAT effluent mass limitations will remove 770 kg/yr of toxic metals over the intermediate option considered, which lacks filtration. Both options are economically achievable. The Agency believes that the incremental removal justifies selecting of filtration as part of BAT model technology. Implementation of the promulgated BAT limitations is expected to result in an estimated capital cost of $0.266 million (March, 1982 dollars) and an estimated annual cost of $0.171 million. EPA is not including any cost for elimination of the catastrophic storm and net precipitation allowances based on its elimination from BPT in 1980.

WASTEWATER DISCHARGE RATES

Important production operations in the primary electrolytic copper refining subcategory are electrolytic refining and casting. Both of these operations are potential sources of wastewater and are evaluated to establish effluent limitations for the subcategory.

Specific wastewater streams associated with the primary electrolytic copper refining subcategory are cathode and anode rinsing wastewater, spent electrolyte, casting contact cooling waste water, and casting wet air pollution control wastewater. Table X-2 (page 1188) lists the production normalized wastewater discharge rates allocated at BAT for these wastewater streams. The values represent the best existing practices of the subcategory, as determined from the analysis of dcp.

ANODE AND CATHODE RINSE WASTEWATER

The BAT wastewater discharge allowance is not provided for anode and cathode rinsing. Six of the 14 primary copper refining facilities reported this waste stream. Five of these plants practice total recycle or reuse of this waste stream, while only one plant discharges the rinsing wastewater. The BAT discharge rate is based on the five plants who do not discharge this waste water.

SPENT ELECTROLYTE

No BAT discharge allowance was provided for spent electrolyte in the proposed regulation. The BAT discharge rate was based on the 13 plants that did not discharge spent electrolyte.

Data supplied to the Agency through comments and Section 308 requests indicate spent electrolyte cannot be recycled 100 percent after electrowinning for some plants. Recycle rates are highly dependent on raw materials and contaminate levels in the anode. As copper is released into solution from the anode, impurities contained in the anode are also released into solution. Several of these impurities, such as silver, gold, lead, and selenium are insoluble in the electrolyte and settle to the bottom of the electrolytic cell. Soluble impurities contained in the cathode consist primarily of bismuth, antimony, and iron. Purity of the cathode copper is very dependent on the concentration of impurities in the electrolyte. Therefore, a portion of the electrolyte is bled from the system and processed in an electrowinning circuit followed by nickel sulfate recovery. In certain instances, raw materials may contain minimal concentrations of nickel making nickel sulfate recovery inappropriate. The bleed rate could be decreased so that nickel concentrations increase and nickel sulfate recovery can be used. However, this will concentrate the bismuth, antimony, and iron impurities and affect product purity. For these reasons, the Agency is modifying the proposed zero discharge requirement for spent electrolyte. The BAT discharge rate is based on the only plant that discharges this wastewater source, and it is equal to 49 l/kkg (12 gal/ton) of cathode copper production.

CASTING CONTACT COOLING WASTEWATER

Nine of the 14 copper refining plants reported this waste stream. Recycle of this waste stream is practiced at five of these plants. Two plants reported total recycle of their casting contact cooling water; however, three plants reported discharging a bleed stream. Wastewater rates for casting contact cooling are presented in Table V-2 (page 1143). The BAT discharge rate is based on the mean normalized discharge flow of the three plants that recycle and discharge a bleed stream (plants 215, 216, and 217). The BAT discharge rate is 498 l/kkg (119 gal/ton) of casting production.

CASTING WET AIR POLLUTION CONTROL

Only one of the 14 copper refining plants reported the use of a casting scrubber. This plant achieves zero discharge of the scrubbing wastewater by deep well injection. Since only one plant uses casting wet air pollution control and this plant is a zero discharger, no BAT discharge allowance is provided for casting wet air pollution control.

BY-PRODUCT RECOVERY

No BAT wastewater discharge allowance is provided for by-product recovery. Two of the three plants which recover by-products from electrolytic copper refining do not discharge wastewater. The single discharging plant generates bleed streams from scrubbers and casting contact cooling associated with by-product recovery after electrowinning. The scrubber is used to control sulfur dioxide (SO_2) emissions from fusion kilns. The scrubber water is not recycled but is discharged to the plant wastewater treatment system. However, the scrubber wastewater flow rate comprises less than one percent of the total plant regulatory flow and is thus considered negligible. Contact cooling water used in casting dore anodes is also discharged to the plant wastewater treatment system. However, the Agency believes there is no need to treat casting contact cooling water from by-product recovery. EPA sampled casting contact cooling water from similar operations at a secondary precious metals plant in the nonferrous metals manufacturing category. The pollutant loadings in this waste water are insignificant compared to the other waste streams selected. The sampling data are presented in the secondary precious metals supplemental development document. Wastewater use and discharge rates for by-product recovery are presented in Table V-4 (page 1142). EPA believes that the solution from electrowinning can be reused in electrolytic refining. In addition, EPA received no comments questioning the proposed zero discharge allowance for this waste stream. For these reasons, and because zero discharge from by-product recovery is demonstrated by two of three plants, EPA has not provided a discharge allowance for by-product recovery.

REGULATED POLLUTANT PARAMETERS

In implementing the terms of the Consent Agreement in NRDC v. Train, Op. Cit., and 33 U.S.C. 1314 (b) (2) (A and B) (1976), the Agency placed particular emphasis on the toxic pollutants. The raw wastewater concentrations from individual operations and the subcategory as a whole were examined to select certain pollutants and pollutant parameters for consideration for limitation. This examination and evaluation, presented in Section VI, concluded that 11 pollutants and pollutant parameters are present in primary electrolytic copper refining wastewaters at concentrations that can be effectively reduced by identified treatment technologies. (Refer to Section VI).

However, the cost associated with analysis for toxic metal pollutants has prompted EPA to develop an alternative method for regulating and monitoring toxic pollutant discharges from the nonferrous metals manufacturing category. Rather than developing specific effluent mass limitations and standards for each of the toxic metals found at treatable concentrations in the raw waste waters from a given subcategory, the Agency is promulgating effluent mass limitations only for those pollutants generated in the greatest quantities as shown by the pollutant reduction benefit analysis. The pollutants selected for specific limitation are listed below:

115. arsenic
120. copper
124. nickel

By establishing limitations and standards for these selected toxic metal pollutants, dischargers are expected to attain the same degree of control over toxic metal pollutants as they would have been required to achieve had all the toxic metal pollutants been directly limited.

This approach is justified technically since the treatable concentrations used for lime precipitation and sedimentation technology are based on optimized treatment for concomitant multiple metals removal. Thus, even though metals have somewhat different theoretical solubilities, they will be removed at very nearly the same rate in a lime precipitation and sedimentation treatment system operated for multiple metals removal. Filtration as part of the technology basis is likewise justified because this technology removes metals non-preferentially.

The following toxic pollutants are excluded from limitation on the basis that they are effectively controlled by the limitations developed for arsenic, copper, and nickel:

119. chromium
122. lead
126. silver
128. zinc

The pollutant parameters proposed for limitation were copper, lead, and nickel. However, with the addition of a spent electrolyte discharge, the pollutant arsenic has been substituted for lead. Analytical data available to the Agency show arsenic concentrations in spent electrolyte exceeding 100 mg/l. In fact, arsenic is second to copper in mass generated and discharged by this subcategory. Arsenic limitations are also added to allow for central treatment with copper acid plant wastewaters where arsenic is a regulated pollutant parameter. As discussed above, lead will be effectively controlled by the limitations developed for arsenic, copper, and nickel based on optimized treatment for concomitant multiple metals removal. Therefore, the promulgated regulation limits three pollutants, copper, nickel, and arsenic.

STORMWATER AND PRECIPITATION ALLOWANCES

The 1975 BAT effluent limitations included net precipitation and catastrophic storm allowances. Primary copper smelters were allowed a discharge of process wastewater which is equivalent to the volume of precipitation that falls within the wastewater impoundment in excess of that attributable to the 25-year, 24-hour rainfall event, when such event occurs. In addition, smelters were allowed to discharge a volume of process wastewater on a monthly basis that is equal to the net difference between the rainfall falling on the impoundment and the mean evaporation from the pond water surface. This monthly discharge was subject to concentration-based standards, whereas the catastrophic storm was not subject to any effluent limitations.

The 1975 BAT regulation for refineries not located on-site with smelters and in areas of net evaporation required discharge standards similar to the BAT primary copper smelting limitations. For refineries located in areas of net precipitation, a constant discharge of refining wastewater was allowed, subject to mass limitations.

EPA modified the primary copper smelting and electrolytic refining storm water and precipitation allowances for BPT in 1980 (refer to Section IX). However, no modifications were made to BAT in that rule. Wastewater generated at primary copper smelters is due primarily to slag granulation and anode casting contact cooling, which can be recycled or reused in other plant processes. There is no monthly allowance for net precipitation from cooling impoundments because they require much smaller surface areas than evaporative impoundments. The Agency is, however, retaining the catastrophic storm water allowances for the 25-year, 24-hour storm event for the primary copper smelting subcategory.

For primary electrolytic copper refining, no stormwater discharge allowances are allocated at BAT. The revised BAT effluent limitations, however, allow a discharge of process wastewater subject to limitations based on sulfide precipitation and pressure filtration (where appropriate), followed by lime precipitation, sedimentation, and filtration. This technology is not as affected by rainfall events because the storm water does not enter the water processing circuits. Therefore, a storm allowance is not provided for the primary electrolytic copper refining subcategory.

EFFLUENT LIMITATIONS

The treatment performance achievable by application of the BAT technology is summarized in Table VII-21 of Vol. 1 (page 248). These treatment performance concentrations (both one day maximum and monthly average) are multiplied by the BAT normalized discharge flows summarized in Table X-3 (page 1191) to calculate the mass of pollutants allowed to be discharged per mass of product. The results of these calculations in milligrams of pollutant per kilogram of product represent the BAT effluent limitations for the primary electrolytic copper refining subcategory.

TABLE X-1

POLLUTANT REMOVAL ESTIMATES FOR PRIMARY COPPER ELECTROLYTIC REFINING DIRECT DISCHARGERS

POLLUTANT	TOTAL RAW WASTE (kg/yr)	OPTION B DISCHARGED (kg/yr)	OPTION B REMOVED (kg/yr)	OPTION C DISCHARGED (kg/yr)	OPTION C REMOVED (kg/yr)
Arsenic	1,334.6	692.5	642.1	47.1	1,287.5
Chromium	8.5	8.5	0.0	8.5	0.0
Copper	379.6	80.3	299.3	54.0	325.6
Lead	15.6	15.6	0.0	11.1	4.5
Nickel	46,710.4	102.5	46,607.9	30.5	46,679.9
Silver	1.4	1.4	0.0	1.4	0.0
Selenium	31.2	31.2	0.0	27.7	3.5
Zinc	457.8	45.7	412.1	31.9	425.9
TOTAL TOXIC METALS	48,939.0	977.7	47,961.3	212.1	48,726.9
TSS	49,945.7	1,662.0	48,283.7	360.1	49,585.6
TOTAL CONVENTIONALS	49,945.7	1,662.0	48,283.7	360.1	49,585.6
TOTAL POLLUTANTS	98,884.7	2,639.7	96,245.0	572.2	98,312.5
FLOW (l/yr)		138,500,000		138,500,000	

NOTE: TOTAL TOXIC METALS - Arsenic + Chromium + Copper + Lead + Nickel + Silver + Selenium + Zinc
TOTAL CONVENTIONALS - TSS
TOTAL POLLUTANTS - Total Toxic Metals + Total Conventionals

OPTION B - Lime Precipitation, Sedimentation, and In-process Flow Reduction
OPTION C - Option B, plus Sulfide Precipition and Pressure Filtration Preliminary Treatment (at one plant), and Multimedia Filtration

TABLE X-2

BAT WASTEWATER DISCHARGE RATES FOR THE PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

Wastewater Stream	Discharge Rate l/kkg	Discharge Rate gal/ton	Production Normalizing Parameter
Anode and cathode rinse water	0	0	Cathode copper production
Spent electrolyte	49	12	Cathode copper production
Casting contact cooling water	498	119	Copper cast
Casting wet air pollution control	0	0	Copper cast
By-product recovery	0	0	By-product production

Table X-3

BAT EFFLUENT LIMITATIONS FOR THE PRIMARY COPPER ELECTROLYTIC REFINING SUBCATEGORY

(a) Casting Contact Cooling

Metric Units - mg/kg of copper cast
English Units - lbs/million lbs of copper cast

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.692	0.309
Chromium	0.184	0,075
Copper*	0.638	0.304
Lead	0.139	0,065
Nickel*	0.274	0.184
Silver	0.144	0,060
Zinc	0.508	0.209

(b) Anode and Cathode Rinse

Metric Units - mg/kg of cathode copper production
English Units - lbs/million lbs of cathode copper production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000

(c) Spent Electrolyte

Metric Units - mg/kg of cathode copper production
English Units - lbs/millions lbs of cathode copper production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.068	0.031
Chromium	0.018	0.007
Copper*	0.063	0.030
Lead	0.014	0.006
Nickel*	0.027	0.018
Silver	0.014	0.006
Zinc	0.050	0.021

(d) Casting Wet Air Pollution Control

Metric Units - mg/kg of casting production
English Units - lbs/million lbs of casting production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000

(e) By-Product Recovery

Metric Units - mg/kg of product recovered from electrolytic slimes processing
English Units - lbs/million lbs of product recovered from electrolytic slimes processing

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000

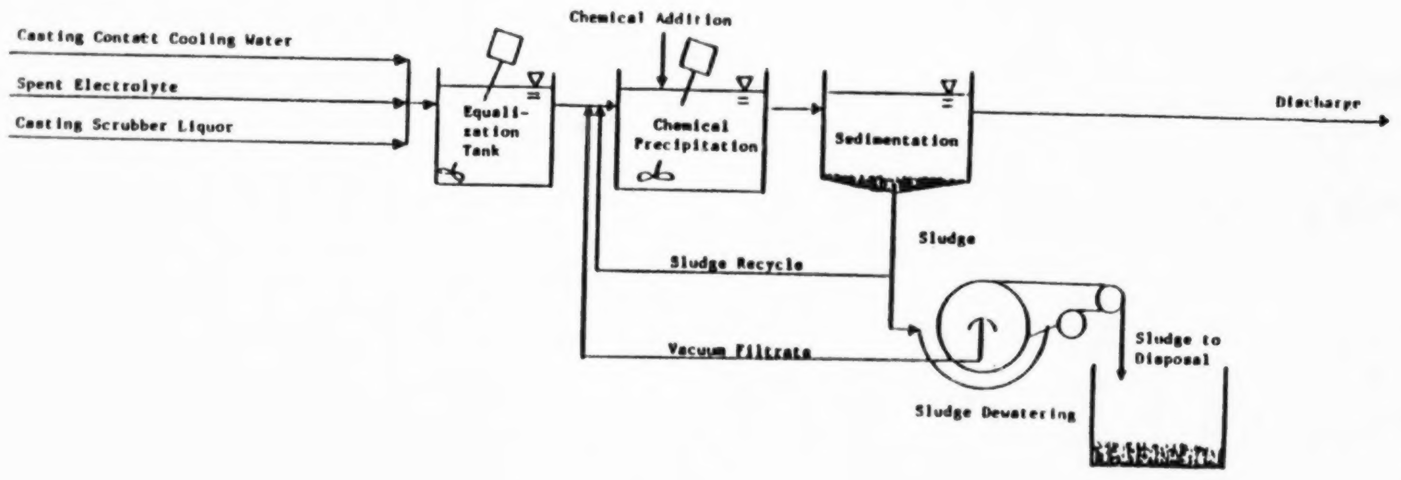
Casting Contact Cooling Water
Spent Electrolyte
Casting Scrubber Liquor
Equalization Tank
Chemical Addition
Chemical Precipitation
Sedimentation
Discharge
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge Dewatering
Sludge to Disposal

Figure X-1

BAT TREATMENT SCHEME OPTION A
PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

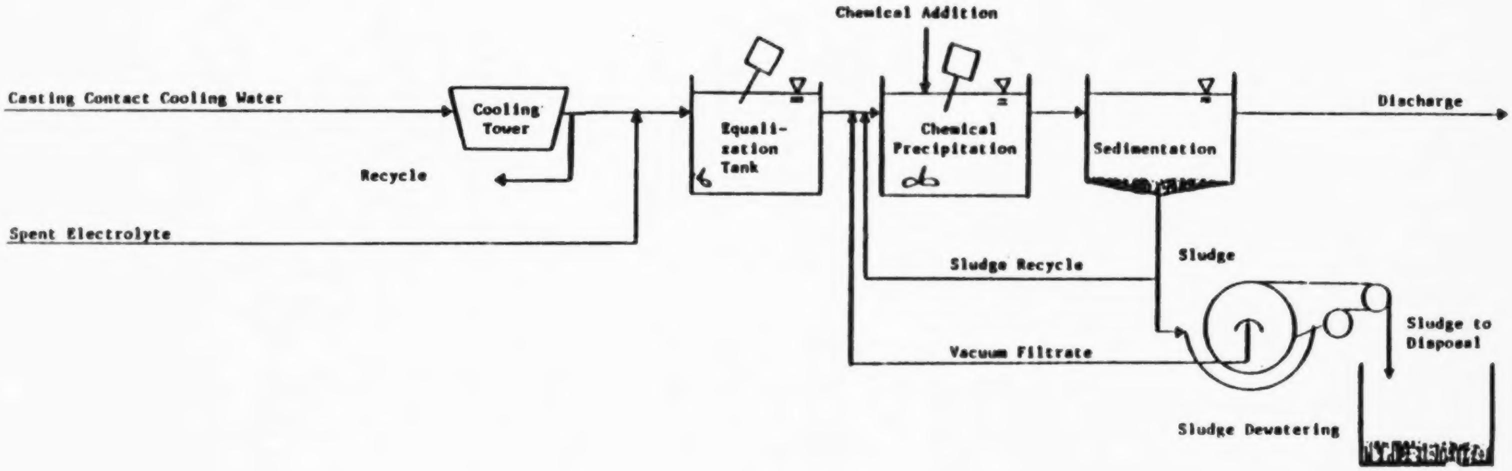
Casting Contact Cooling Water
Cooling Tower
Recycle
Spent Electrolyte
Equalization Tank
Chemical Addition
Chemical Precipitation
Sedimentation
Discharge
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge to Disposal
Sludge Dewatering

Figure X-2

BAT TREATMENT SCHEME OPTION B
PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

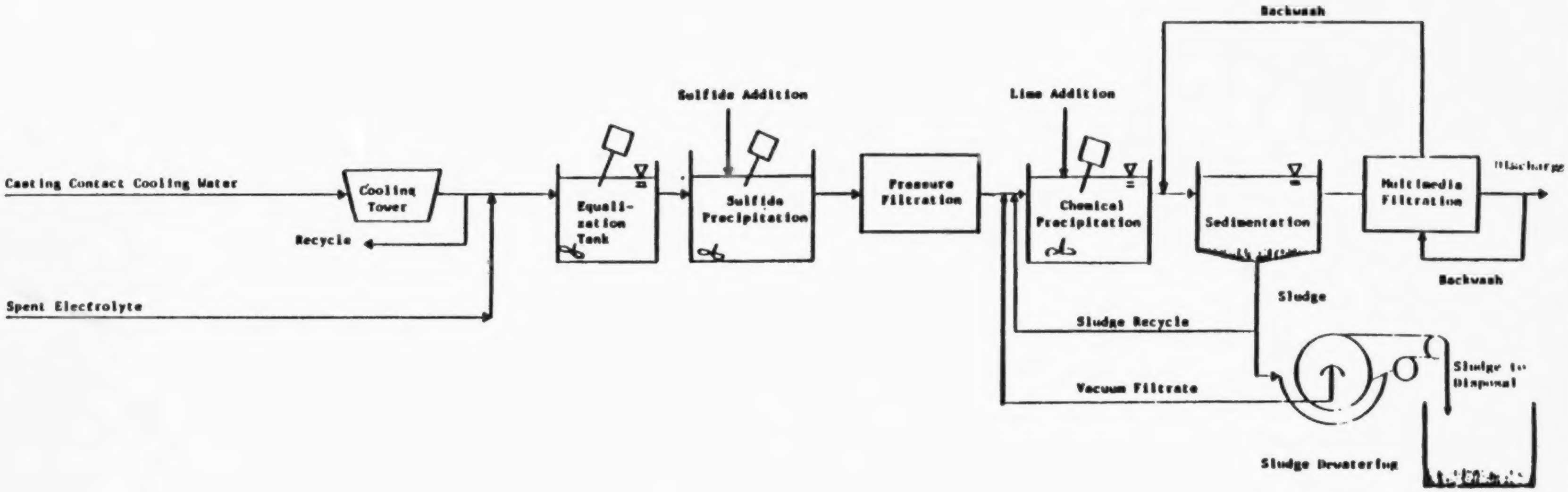
Casting Contact Cooling Water
Cooling Tower
Recycle
Spent Electrolyte
Equalization Tank
Sulfide Addition
Sulfide Precipitation
Pressure Filtration
Lime Addition
Chemical Precipitation
Backwash
Sedimentation
Multimedia Filtration
Discharge
Backwash
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge to Disposal
Sludge Dewatering

Figure X-3

BAT TREATMENT SCHEME OPTION C
PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology (BDT). New plants have the opportunity to design the best and most efficient production processes and wastewater treatment technologies without facing the added costs and restrictions encountered in retrofitting an existing plant. Therefore, Congress directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible. This section describes technologies for treatment of wastewater from new sources, and presents mass discharge standards of regulated pollutants for NSPS based on the selected treatment technology.

TECHNICAL APPROACH TO BDT

All of the treatment technology options applicable to a new source were previously considered for BAT options. Three options were considered for BDT for the primary electrolytic copper refining subcategory. The options considered for BDT are identical to the BAT options discussed in Section X. The treatment technologies used for the three BDT options are

OPTION A

- Chemical precipitation and sedimentation

OPTION B

- Chemical precipitation and sedimentation
- Flow reduction

OPTION C

- Sulfide precipitation and pressure filtration (for one plant only)
- Chemical precipitation and sedimentation
- Flow reduction
- Multimedia filtration

Partial or complete reuse or recycle of wastewater is an essential part of Options B and C. Reuse or recycle can precede or follow end-of-pipe treatment.

BDT OPTION SELECTION

EPA is promulgating the best available demonstrated technology for the primary electrolytic copper refining subcategory equal to the chemical precipitation, sedimentation, and filtration technology at BAT. Additional flow reduction and more stringent treatment technologies are not demonstrated or readily transferable to the primary electrolytic copper refining subcategory.

REGULATED POLLUTANT PARAMETERS

The Agency has no reason to believe that the pollutants that will be found in treatable concentrations in processes within new sources will be any different than with existing sources. Accordingly, pollutants and pollutant parameters selected for limitation under NSPS are identical to those selected for BAT with the addition of the conventional pollutant parameters TSS and pH.

NEW SOURCE PERFORMANCE STANDARDS

The NSPS discharge flows are the same as the BAT discharge flows for all processes associated with the primary electrolytic copper refining subcategory. The discharge flows are listed in Table XI-1 (page 1202). The mass of pollutant allowed to be discharged per mass of product is calculated by multiplying the achievable treatment concentration (mg/l) by the normalized wastewater discharge flow (l/kkg). The BDT achievable treatment concentrations are identical to the BAT achievable treatment concentrations and are presented in Table VII-21 of Vol. 1 (page 248). New source performance standards, as determined from the above procedure, are shown in Table XI-2 (page 1203).

TABLE XI-1

NSPS WASTEWATER DISCHARGE RATES FOR THE PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

Wastewater Stream	Discharge Rate l/kkg	Discharge Rate gal/ton	Production Normalizing Parameter
Anode and cathode rinse water	0	0	Cathode copper production
Spent electrolyte	49	12	Cathode copper production
Casting contact cooling water	498	119	Copper cast
Casting wet air pollution control	0	0	Copper cast
By-product recovery	0	0	By-product production

TABLE XI-2

NEW SOURCE PERFORMANCE STANDARDS FOR THE PRIMARY COPPER ELECTROLYTIC REFINING SUBCATEGORY

(a) Casting Contact Cooling

Metric Units - mg/kg of copper cast
English Units - lbs/million lbs of copper cast

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.692	0.309
Chromium	0.184	0,075
Copper*	0.638	0.304
Lead	0.139	0,065
Nickel*	0.274	0.184
Silver	0.144	0,060
Zinc	0.508	0.209
TSS*	7.470	5.976
pH*	Within the range of 7.0 to 10.0 at all times	

(b) Anode and Cathode Rinse

Metric Units - mg/kg of cathode copper production
English Units - lbs/million lbs of cathode copper production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000
TSS*	0.000	0.000
pH*	Within the range of 7.0 to 10.0 at all times	

(c) Spent Electrolyte

Metric Units - mg/kg of cathode copper production
English Units - lbs/million lbs of cathode copper production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.068	0.031
Chromium	0.018	0.007
Copper*	0.063	0.030
Lead	0.014	0.006
Nickel*	0.027	0.018
Silver	0.014	0.006
Zinc	0.050	0.021
TSS*	0.735	0.588
pH*	Within the range of 7.0 to 10.0 at all times	

(d) Casting Wet Air Pollution Control

Metric Units - mg/kg of copper casting production
English Units - lbs/million lbs of copper casting production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000
TSS*	0.000	0.000
pH*	Within the range of 7.0 to 10.0 at all times	

(e) By-Product Recovery

Metric Units - mg/kg of product recovered from electrolytic slimes processing
English Units - lbs/million lbs of product recovered from electrolytic slimes processing

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000
TSS*	0.000	0.000
pH*	Within the range of 7.0 to 10.0 at all times	

SECTION XII

PRETREATMENT STANDARDS

INTRODUCTION

Section 307(b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES), which must be achieved within three years of promulgation. PSES are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of publicly owned treatment works (POTW). The Clean Water Act of 1977 requires pretreatment for pollutants, such as toxic Metals, that limit POTW sludge management alternatives. Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect discharge facilities, like new direct discharge facilities, have the opportunity to incorporate the best available demonstrated technologies, including process changes, in-plant controls, and end-of-pipe treatment technologies, and to use plant site selection to ensure adequate treatment system installation. Pretreatment standards are to be technology-based, analogous to the best available technology for removal of toxic pollutants.

This section describes the control and treatment technologies for pretreatment of process wastewaters from existing sources and new sources in the primary electrolytic copper refining subcategory. Pretreatment standards for regulated pollutants are presented based on the selected treatment technology.

TECHNICAL APPROACH TO PRETREATMENT

Before proposing pretreatment standards, the Agency examines whether the pollutants discharged by the industry pass through the POTW or interfere with the POTW operations or its chosen sludge disposal practices. In determining whether pollutants pass through a well-operated POTW, achieving secondary treatment, the Agency compares the percentage of a pollutant removed by POTW with the percentage removed by direct dischargers applying the best available technology economically achievable. A pollutant is deemed to pass through the POTW when the average percentage removed nationwide by well-operated POTW meeting secondary treatment requirements, is less than the percentage removed by direct dischargers complying with BAT effluent limitations guidelines for that pollutant (see 46 FR 9415-16, January 28, 1981). This definition of pass through satisfies two competing objectives set by Congress: (1) that standards for indirect dischargers be equivalent to standards for direct dischargers, while at the same time, (2) that the treatment capability and performance of the POTW be recognized and taken into account in regulating the discharge of pollutants from indirect dischargers.

The Agency compares percentage removal rather than the mass or concentration of pollutants discharged because the latter would not take into account the mass of pollutants discharged to the POTW from non-industrial sources nor the dilution of the pollutants in the POTW effluent to lower concentrations due to the addition of large amounts of non-industrial wastewater.

PRETREATMENT STANDARDS FOR EXISTING SOURCES

There are no indirect discharging primary electrolytic copper refining plants in the United States. Consequently, the Agency has elected to not promulgate pretreatment standards for existing sources.

PRETREATMENT STANDARDS FOR NEW SOURCES

Options for pretreatment of wastewaters are based on increasing the effectiveness of end-of-pipe treatment technologies. All in-plant changes and applicable end-of-pipe treatment processes have been discussed previously in Sections X and XI. The treatment options for PSNS, therefore, are the same as the options discussed in Section X.

A description of each option is presented in Section X, while a more detailed discussion, including pollutants controlled by each treatment process and expected effluent quality for each option, is presented in Section VII of the General Development Document.

Treatment technologies used for the PSNS options for the primary electrolytic copper refining subcategory are:

Option A

- Chemical precipitation and sedimentation

Option B

- Chemical precipitation and sedimentation
- Flow reduction

Option C

- Chemical precipitation and sedimentation
- Flow reduction
- Multimedia filtration

PSNS OPTION SELECTION

EPA has selected chemical precipitation, sedimentation, in-process flow reduction, and filtration (Option C) as the technology basis for PSNS for the primary electrolytic copper refining subcategory. As with NSPS, EPA believes that the addition of filtration is feasible for new indirect dischargers. No additional flow reduction is required for PSNS because the only other applicable flow reduction technology, reverse osmosis, is not demonstrated or clearly transferable for nonferrous metals manufacturing wastewater.

REGULATED POLLUTANT PARAMETERS

With the exception of conventional pollutant parameters TSS and pH, the toxic pollutants and pollutant parameters selected for limitation, in accordance with the rationale of Sections VI and X, are identical to those selected for limitation for BAT. PSNS prevents the pass-through of arsenic, copper and nickel.

PRETREATMENT STANDARDS

The PSNS discharge flows for the primary electrolytic copper refining subcategory are the same as the BAT discharge flows for all processes. The discharge flows are listed in Table XII-1 (page 1204). The mass of pollutant allowed to be discharged per mass of product is calculated by multiplying the PSNS achievable treatment concentration (mg/l) by the normalized wastewater discharge flow (l/kkg). The PSNS achievable treatment concentrations are identical to the BAT achievable treatment concentrations and are presented in Table VII-21 of Vol. 1 (page 248). Pretreatment standards for new sources, as determined from the above procedure, are shown in Table XII-2 (page 1205).

Mass-based standards are promulgated for the primary electrolytic copper refining subcategory to ensure that the standards are achieved by means of pollutant removal rather than by dilution. They are particularly important since the standards are based upon flow reduction. Pollutant limitations associated with flow reduction cannot be measured any other way but as a reduction of mass discharged.

TABLE XII-1

PSNS WASTEWATER DISCHARGE RATES FOR THE PRIMARY ELECTROLYTIC COPPER REFINING SUBCATEGORY

Wastewater Stream	Discharge Rate l/kkg	Discharge Rate gal/ton	Production Normalizing Parameter
Anode and cathode rinse water	0	0	Cathode copper production
Spent electrolyte	49	12	Cathode copper production
Casting contact cooling water	498	119	Copper cast
Casting wet air pollution control	0	0	Copper cast
By-product recovery	0	0	By-product production

TABLE XII-2

PRETREATMENT STANDARDS FOR NEW SOURCES FOR THE PRIMARY COPPER ELECTROLYTIC REFINING SUBCATEGORY

(a) Casting Contact Cooling

Metric Units - mg/kg of copper cast
English Units - lbs/million lbs of copper cast

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.692	0.309
Chromium	0.184	0,075
Copper*	0.638	0.304
Lead	0.139	0,065
Nickel*	0.274	0.184
Silver	0.144	0,060
Zinc	0.508	0.209

(b) Anode and Cathode Rinse

Metric Units - mg/kg of cathode copper production
English Units - lbs/million lbs of cathode copper production

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000

(c) Spent Electrolyte

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of cathode copper production English Units - lbs/million lbs of cathode copper production	
Arsenic*	0.068	0.031
Chromium	0.018	0.007
Copper*	0.063	0.030
Lead	0.014	0.006
Nickel*	0.027	0.018
Silver	0.014	0.006
Zinc	0.050	0.021

(d) Casting Wet Air Pollution Control

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of casting production English Units - lbs/million lbs of casting production	
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000

(e) By-Product Recovery

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
	Metric Units - mg/kg of product recovered from electrolytic slimes processing English Units - lbs/million lbs of product recovered from electrolytic slimes processing	
Arsenic*	0.000	0.000
Chromium	0.000	0.000
Copper*	0.000	0.000
Lead	0.000	0.000
Nickel*	0.000	0.000
Silver	0.000	0.000
Zinc	0.000	0.000

SECTION XIII

BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY

EPA is not promulgating best conventional pollutant control technology(BCT) for the primary electrolytic copper refining subcategory at this time.

NONFERROUS METALS MANUFACTURING POINT SOURCE CATEGORY

DEVELOPMENT DOCUMENT SUPPLEMENT

for the

Secondary Copper Subcategory

William K. Reilly
Administrator

Rebecca Hanmer
Acting Assistant Administrator for Water

Martha Prothro, Director
Office of Water Regulations and Standard

Thomas P. O'Farrell, Director
Industrial Technology Division

Ernst P. Hall, P.E., Chief
Metals Industry Branch
and
Technical Project Officer

May 1989

U.S. Environmental Protection Agency
Office of Water
Office of Water Regulations and Standards
Industrial Technology Division
Washington, D. C. 20460

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SECONDARY COPPER SUBCATEGORY

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SECTION I

SUMMARY

On February 27, 1975, EPA promulgated technology-based effluent limitations for the secondary copper subcategory of the Nonferrous Metals Manufacturing Point Source Category. Effluent limitations were established based on the best practicable control technology currently available (BPT) and best available technology economically achievable (BAT). Under these limitations, the discharge of process wastewater pollutants into navigable waters was prohibited with the following exceptions. For the BPT effluent limitations, discharge without limitation was allowed for a volume of process wastewater equivalent to the volume of stormwater in excess of that attributable to a 10-year, 24-hour rainfall event falling on a wastewater cooling impoundment. The BAT effluent limitations also contain the stormwater exemption except the storm is a 25-year, 24-hour rainfall event. For both the BPT and BAT effluent limitations, discharge, subject to concentration-based limitations, was allowed for a volume of process wastewater equal to the net monthly precipitation on the wastewater cooling impoundment.

On December 15, 1976, (41 FR 54850) EPA promulgated pretreatment standards for existing sources (PSES) for the secondary copper subcategory. These standards allowed a continuous discharge of process waste- water to publicly owned treatment works (POTW) subject to concentration-based standards for oil and grease, copper, and cadmium. These PSES were based on lime precipitation and sedimentation treatment technology.

In the March 1984 rulemaking (49 FR 8742), EPA promulgated modifications to BAT, and PSES and promulgated NSPS and PSNS for the secondary copper subcategory pursuant to the provisions of Sections 301, 304, 306, and 307 of the Clean Water Act as amended. This supplement provides a compilation and analysis of the background material used to develop these effluent limitations and standards.

The secondary copper subcategory is comprised of 31 plants. Of the 31 plants, five discharge directly to rivers, lakes, or streams; six discharge to publicly owned treatment works (POTW); and 20 achieve zero discharge of process wastewater pollutants.

EPA first studied the secondary copper subcategory to determine whether differences in raw materials, final products, manufacturing processes, equipment, age and size of plants, and water usage required the development of separate effluent limitations and standards for different segments of the subcategory. This involved a detailed analysis of wastewater discharge and treated effluent characteristics, including: (1) the sources and volume of water used, the processes used, and the sources of pollutants and wastewaters in the plant; and (2) the

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constituents of waste waters, including toxic pollutants.

Several distinct control and treatment technologies (both in-plant and end-of-pipe) applicable to the secondary copper subcategory were identified. The Agency analyzed both historical and newly generated data on the performance of these technologies. EPA also studied various flow reduction and complete recycle techniques reported in the data collection portfolios (dcp) and plant visits.

Based on consideration of the above factors, EPA identified various control and treatment technologies which formed the basis for BAT and selected control and treatment appropriate for each set of standards and limitations. The mass limitations and standards for BPT, BAT, NSPS, PSES, and PSNS are presented in Section II.

For BAT, the Agency is eliminating the discharge allowance for net monthly precipitation on cooling impoundments. The BAT effluent limitations will still allow a discharge for stormwater resulting from the 25-year, 24-hour rainfall event. EPA is eliminating the net precipitation discharge for BAT because these limitations are based on the use of cooling ponds rather than evaporative impoundments. Cooling impoundments require much smaller surface areas than the evaporative impoundments for which the net precipitation discharge was allowed.

Costs for cooling towers were developed for BAT in the 1975 rulemaking when a plant had insufficient existing cooling impoundment capacity or cooling impoundments were not feasible due to space limitations. EPA believes that secondary copper plants can accommodate the small volume of water resulting from net precipitation on cooling impoundments. There is no cost associated with the promulgated BAT effluent limitations.

For NSPS, EPA is promulgating a standard prohibiting the discharge of process wastewater pollutants to waters of the United States. In selecting NSPS, EPA recognizes that new plants have the opportunity to implement the best and most efficient manufacturing processes and treatment technology. EPA believes that new sources can be constructed with cooling towers rather than impoundments and clarification devices rather than settling ponds. The Agency is thus eliminating the allowance for catastrophic stormwater discharge provided at BAT.

For PSES, EPA is promulgating a standard prohibiting the introduction of process wastewater pollutants into POTW. The technology basis for the promulgated PSES is lime precipitation and sedimentation with cooling towers and holding tanks to achieve zero discharge of process wastewater pollutants. The PSES will allow a discharge resulting from the 25-year, 24-hour rainfall event with no net precipitation allowance. EPA believes that the costs associated with installation and operation of cooling towers and holding tanks for indirect dischargers will be insignificant. In addition, costs for cooling towers and holding tanks were considered during the 1976 PSES rulemaking. At that time EPA concluded that the additional cost was not significant.

For PSNS, EPA is also promulgating a standard prohibiting the introduction of process wastewater pollutants into POTW. There is no allowance for discharge from a catasthrophic rainfall event. The Agency believes that all of the factors set forth above for as a basis for PSES apply. In addition, a new source has the option of selecting new technology and locations which are conducive to the achievement of the standard without the need for a catastrophic rainfall allowance.

SECTION II

CONCLUSIONS

The secondary copper subcategory has been divided into seven subdivisions for the purpose of effluent limitations and standards. These subdivisions are:

(a) Residue concentration,
(b) Slag granulation,
(c) Reverberatory and rotary furnace wet air pollution control,
(d) Spent electrolyte,
(e) Scrap anode rinsing,
(f) Casting contact cooling, and
(g) Casting wet air pollution control.

EPA promulgated BPT effluent limitations for the secondary copper subcategory on February 27, 1975 (46 FR 8513) as Subpart F of 40 CFR Part 421. Promulgated BPT for the secondary copper subcategory is no discharge of all process wastewater pollutants with two exceptions. Facilities in the secondary copper subcategory may discharge without restriction the volume of water falling within a cooling impoundment in excess of the 10-year, 24-hour precipitation event, when a storm of at least that magnitude occurs. Further, they can discharge, subject to concentration-based effluent limitations, a volume of water equal to the difference between monthly precipitation and evaporation on the cooling impoundment in that month. Process wastewater discharged pursuant to the net precipitation allowance must comply with the following concentration-based effluent limitations:

BPT EFFLUENT LIMITATIONS

Pollutant or pollutant property	Maximum for any one day	Average of Daily Values for 30 Consecutive days shall not exceed
	Metric Units (mg/l) English Units (ppm)	
Total Suspended Solids	50	25
Copper	0.5	0.25
Zinc	10	5
Oil and Grease	20	10
pH	Within the range of 6.0 to 9.0	

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EPA is promulgating BAT effluent limitations for the secondary copper subcategory that prohibits the discharge of all process wastewater pollutants, subject to a discharge allowance for catastrophic storm water. Facilities in the secondary copper subcategory may discharge the volume of process wastewater that exceeds the volume of precipitation that falls within an effluent cooling impoundment in excess of the 25-year, 24-hour storm when a rainfall event of at least that magnitude occurs.

EPA is promulgating NSPS for the secondary copper subcategory that prohibits the discharge of all process wastewater pollutants to waters of the United States.

EPA is promulgating PSES for the secondary copper subcategory that prohibits the discharge of all process wastewater pollutants to POTW, subject to a discharge allowance for catastrophic storm water. Facilities in the secondary copper subcategory may discharge without restriction the volume of water that falls within the cooling impoundment in excess of the 25-year, 24-hour storm when a rainfall event of at least that magnitude occurs.

EPA is promulgating PSNS for the secondary copper subcategory that prohibits the discharge of all process wastewater pollutants to POTW.

SECTION III

SUBCATEGORY PROFILE

This section of the secondary copper Subcategory supplement profiles the secondary copper subcategory and describes the raw materials and processes used in smelting and refining secondary copper and copper-base alloys, and presents a profile of the secondary copper subcategory. For a discussion of the purpose, authority, and methodology for this study and a general description of the nonferrous metals manufacturing category, refer to Section III of Vol. I.

DESCRIPTION OF SECONDARY COPPER PRODUCTION

There are a variety of manufacturing processes involved in the production of secondary copper or copper-base alloys. The raw materials and desired end product play an important role in determining the manufacturing process of a particular plant. The principal steps involved in the production of secondary copper and copper-base alloys are tabulated below. Each of these production steps, along with raw materials, is discussed in detail below.

1. Pretreatment of scrap;
2. Smelting of low-grade scrap and residues;
3. Melting, refining, and alloying intermediate-grade copper-base scrap and residues;
4. Refining high-grade copper scrap; and
5. Casting.

RAW MATERIALS

Discarded consumer products, industrial copper-bearing scrap metal (solids) and melting wastes (slags and residues) are the basic raw materials used in secondary copper facilities. About two-thirds of the recycled copper tonnage is in the form of brass and bronze, with the remaining one-third in the form of copper. Additional copper values are recovered from copper-bearing wastes, such as skimmings, grindings, ashes, irony brass and copper residues and slags. The United States Department of Interior has estimated that 60 percent of all copper-base metal is reclaimed as old metal and comes back into production again. The cycle between its original use and recovery is approximately 40 years.

The segregation and classification of scrap metal are important steps in the production of alloyed ingots or pure copper. Segregation of copper-base scrap is done in a preliminary way by the scrap dealer (old scrap) or by the fabrication plant as the scrap is generated (new scrap). The copper-bearing scrap sold to the smelters contains metallic and nonmetallic impurities. Included among these are lead, zinc, tin, antimony, iron, manganese, nickel, chromium, precious metals, and organic-base constituents, such as insulation (plastic and other types), oil, grease, paint, rubber, and antifreeze.

PRETREATMENT OF SCRAP

Before scrap, in the form of solids (metal) and residues, is used by the smelter, various types of pretreatment are performed. The materials are usually presorted by secondary material dealers or shipped directly by foundries and metal shops; however, additional sorting is often done by the smelter to attain tighter control of the alloy constituents and the copper content. The steps used in the pretreatment of scrap depend on the type of scrap being processed. These pretreatment steps are shown schematically in Figure III-1 (page 1240) and are discussed below in the context of the type of scrap being processed.

Stripping

Insulation and lead sheathing are removed from electrical conductors, such as cables, by specially designed stripping machines or by hand. Water is not used or generated during stripping and atmospheric emissions are not generated by this process. The lead is sold, reclaimed, or used in producing copper-base alloys. The organic solid wastes are reclaimed or disposed by burning or other solid waste disposal methods.

Briquetting

Compressing bulky scrap, such as borings, turnings, tubing, thin plate, wire screen, and wire, into small bales compacts the scrap, allows for less storage area, and makes for easier handling and faster melting. The problem of oxidation of the metal is also diminished. Briquetting is carried out by compacting the scrap with hydraulic presses. Water is not used or generated during briquetting and atmospheric emissions are not generated by this process.

Size Reduction

Size reduction is used for all types of scrap materials. Large thin pieces of scrap metal are reduced in size by pneumatic cutters, electric shears, and manual shearing. Tramp iron liberated from the scrap by size reduction is removed from the shredded product magnetically. The iron-free products are usually briquetted for easy handling. Shredding is also used in the separation of insulation on copper wire. The insulation is broken loose from metal by shearing action and removed from the metal by air classification.

When treating bulky metal items, the process produces small quantities of atmospheric emissions, consisting of dusts of approximately the same composition as the metal. Collection of

the dust via dry cyclones or baghouses permits recovery of the metal value.

Crushing

Previously dried, brittle, spongy turnings, borings, and long chips are processed in hammer mills or ball mills. After crushing, tramp iron is removed magnetically. Dust particles consisting of dirt, organic compounds, and finely divided metal are generally collected using dry cyclones.

Residue Concentration

Some secondary copper plants concentrate the copper values in slags and other residues, such as drosses, skimmings, spills, and sweepings, before charging the concentrates into rotary or reverberatory furnaces. Slags may be crushed, screened through a coarse screen to remove trash and lumps of copper, pulverized with a ball mill, and concentrated on a table classifier. The concentrate usually contains 70 to 90 percent copper or copper alloy, and the gangue, or depleted slag, contains 4 or 5 percent copper alloy. The depleted slag is usually retained at the plant site as landfill. Lower grade residues are wet milled and concentrated by gravity and table classifiers.

The concentration of residues is usually done by wet grinding and classifying. The water associated with this processing contains some milling fines as suspended solids and dissolved solids from the soluble components of the residue and metals. To limit water consumption, the water used for milling is recycled from holding tanks or ponds.

Residue Pelletizing and Roll Briquetting

Most small brass and bronze ingot makers (facilities) do not process residues, but actually sell their copper bearing residues to the larger refineries for processing to recover the copper values. Some of the large refineries charge the residues into their cupola or blast furnaces for the recovery of the copper content in the slag or residues.

The fine portions of the copper rich slags or other residues are palletized by adding water and a binder, if necessary, and rolling the material in a disk or drum pelletizer until most of the fines are in the form of small marble size pellets. Although water is used in pelletizing, it is completely consumed during processing and wastewater is not discharged.

Drying

Borings, turnings, and chips from machining are covered with cutting fluids, oils, and greases. These contaminants are removed in the drying process. The scrap is generally heated in a rotary kiln to vaporize and burn the contaminants.

Drying results in the evolution of considerable quantities of hydrocarbons, depending on the amount present in the scrap. The oils, greases, and cutting fluids contain sulfonated and chlorinated hydrocarbons. Therefore, gaseous emissions evolve and are composed of the oxidation products that include sulfur oxides, hydrogen chloride, hydrocarbons, and other combustion products.

The atmospheric emissions are controlled by burning the vaporized fumes in afterburners, which oxidize the hydrocarbons to carbon dioxide and water. Inorganic particulates settle out in the afterburner section. Sulfur oxides and chloride emissions are usually uncontrolled. As such, water is not used or generated during drying.

Burning

Scrap may be covered with paper and organic polymer insulation, such as rubber, polyethylene, polypropylene, or polyvinyl chloride. These materials are usually not removed by stripping. They are most effectively removed from the scrap by the burning process using furnaces, such as rotary kilns.

The burning process generates combustion products such as carbon dioxide and water Emissions from the burning of polyvinyl chloride may contain such gases as phthalic anhydride and hydrogen chloride. Fluorocarbon insulation releases hydrogen fluoride when burned. Many of these gases are highly toxic and corrosive. These gases may be controlled through the use of wet scrubbers, however, no plants in this subcategory report the use of wet scrubbers for controlling burning furnace emissions.

Sweating

Scrap containing low melting point materials, such as radiators, journal bearings, and lead sheathed cables, can be sweated to remove babbitt, lead, and solder as valuable by-products, which would otherwise contaminate a melt. Scrap may be added directly to a melt without sweating if the melt requires substantial amounts of the sweatable constituents. Sweating is done by heating in an oil- or a gas-fired muffle type furnace with a sloped hearth, so that the charge can be kept on the high side and away from the fluid, low melting point components. The molten metal is collected in pots, and the sweated scrap is raked until most of the low melting metals have been freed. The process can be a continuous or a batch operation. Sweating is also done in pots by dumping the scrap into molten alloy, which absorbs the sweated babbitt, lead, or solder. Rotary kilns have been used on small size scrap. The tumbling action aids in removing the molten metals. For items which are difficult to sweat, a reverberatory furnace equipped with a shaking grate is used. Continuous sweating is done in tunnel furnaces that have provisions for solder, lead, and babbitt recovery.

Atmospheric emissions consist of fumes and combustion products originating from antifreeze residues, soldering fluxes, rubber hose remains, and the fuel used to heat the sweat furnace. None of the plants in this subcategory use wet scrubbing for sweating furnaces.

SMELTING OF LOW-GRADE SCRAP AND RESIDUES

Drosses, slags, skimmings, and low-grade copper and brass scrap are processed in blast furnaces or cupola furnaces. These low-grade, copper-bearing materials are melted to separate the copper values from slags or residues and to produce molten metal that can be processed further immediately after recovery, or after being cast into ingots or shot for later use or sale. The smelting process is shown in Figure III-2 (page 1241)

The product of cupola or blast furnace melting is known as black copper or cupola melt. It generally consists of a mixture of copper and variable amounts of most of the common alloying elements such as tin, lead, zinc, nickel, iron, phosphorus, and to a lesser extent arsenic, antimony, aluminum, beryllium, chromium, manganese, silicon, and precious metals. A matte is also formed when sufficient sulfur is present to form a complex copper-iron-nickel-lead sulfide. Other specialty furnaces, such as crucible or induction furnaces, are sometimes used for special alloy production or precious metal recovery.

The charge to the blast or cupola furnace may be in the form of irony brass and copper, fine insulated wire, motor armatures, foundry sweepings, slags, drosses, and many other low-grade materials. Fine materials are pretreated by pelletizing or briquetting to reduce losses in the stack gas. Limestone and mill scale are added as fluxes to produce iron silicate slags (depleted slag). Low sulfur coke is used in cupolas or blast furnaces to reduce matte (copper sulfide) formation.

During the cupola and blast furnace processes, the metallic constituents melt, while the limestone, aluminum, silicon and iron oxides fuse in the smelting zone and form a molten slag, which mixes with the metals. The copper compounds are reduced by the coke. The molten materials flow downward through the coke bed and are collected in a crucible below. After a period of quiescence, the metal and slag form separate layers and are tapped. The slag, containing less than one percent copper value, is granulated with a high pressure water spray or by directing it into a quench pit while still in its molten state. The granulated slag is then sent to a slag pile.

Cupola and blast furnace operations produce large quantities of particulate matter from dusty charge materials, such as fine slags, fine fluxes, and coke ash, as well as metal oxide fumes. These particulates and fumes are controlled through the use of air pollution control devices. Dry air pollution control devices such as baghouse filters and cyclones are currently used to contain these particulates and fumes.

The process of conversion in the secondary copper subcategory can be done in furnaces called converters or in other types of furnaces in which molten metal is contained. The operation is derived from primary copper operation in which the sulfide matte is converted to an oxide-rich copper melt by oxidation with air or oxygen-enriched air. In secondary copper operations, however, only small amounts of sulfide are present in the black copper, but it is heavily contaminated with alloy metals, such as zinc, lead, nickel, iron, manganese, aluminum, tin, antimony, silicon, silver, or other metals and nonmetals contained in the scrap or residues. Since the sulfur content is low in secondary black copper, fuel is required for converting operations; unlike primary copper where the sulfur serves as the fuel.

With the use of converters or converter-oriented operations, the copper value in mixed alloys is reclaimed by oxidizing most of the alloying elements and removing the oxides as a slag. Molten metal is sometimes oxidized in a converter by blowing air through ports in the bottom of the furnace until most of the oxidizable alloying elements and some of the copper are oxidized (blister copper). More commonly, the molten metal in reverberatory or rotary furnaces is oxidized by inserting water cooled lances into the bath and blowing the bath with air or oxygen under a silicate slag cover until the alloy impurities are reduced to the desired level. The slag containing the alloy metal oxides and some copper is removed, and the oxygen in the remaining copper is reduced with charcoal, green wood, natural gas or other reducing agent inserted into the bath. Depending on the extent of reduction, various grades of refined copper are produced. Generally, after conversion, a blister copper is produced that is subsequently refined in the same plant or sold or transported to other plants.

Air emissions from converter furnaces are currently contained through the use of dry air pollution control devices. The control of reverberatory and rotary furnace air emission will be discussed later in this section.

MELTING, REFINING, AND ALLOYING INTERMEDIATE-GRADE COPPER-BASED SCRAP

As shown in Figure III-2 (page 1241), copper-based scrap metals, intermediate-grade copper metal scrap, black and blister copper, and residues with known origin or composition are melted, refined, and alloyed, if necessary, to produce either brass or bronze ingots of specific composition. These same materials are refined further to produce fire refined copper suited for end use or for casting anodes for electrolytic refining. Direct fired reverberatory and rotary furnaces are used to produce the product metals, brass and bronze, and fire refined copper.

In the production of brass and bronze ingots, the extent of refining is usually small, if the scrap is well sorted. If the residues are of known origin (usually a toll recovery operation), refining is also kept to a minimum. In the production of copper, the extent of refining is greater. The chemical principles of refining are applicable to both brass and bronze ingot manufacture and the preparation of fire refined copper.

In the refining step, impurities and other constituents of the charge, present in excess of specifications, are oxidized. Elements, such as iron, manganese, silicon, and aluminum, are normally considered to be contaminants in copper base alloys and must be removed by refining. In the preparation of refined copper, the alloying elements common to brass and bronze must also be removed. The methods used in refining vary with the type of furnace, the types of scrap in the charge, as well as the type of product being produced.

The reverberatory or rotary furnace is charged with scrap metal at the start of the heat and at intervals during the melt down period. Air is blown into the molten metal bath with lances in order to oxidize metals in near accordance with their position in the electromotive series. Thus, iron, manganese, aluminum, and silicon are oxidized. In the production of refined copper, the blowing is for a longer duration, since most of the metal elements must be removed.

The oxidized metals form a slag layer on the surface of the melt, since the oxides have a lower density than the molten metal. These oxides combine with the slag cover, which is usually added to aid in the removal of the oxidized impurities. Borax, slaked lime or hydrated lime, glass or silica, soda ash, and caustic soda are all used as fluxes to modify the characteristics of the slag cover. The most common material used by the brass and bronze smelters is anhydrous rasorite, a sodium borate flux ($Na_2B_4O_7$), which has a great affinity for metal oxides and siliceous materials. The slag cover protects the molten metal surface from unwanted oxidation and reduces volatilization of zinc.

To oxidize or degasify, as well as to alloy, a brass or bronze melt, metal fluxing agents are added to the melt. In almost all cases, these melt modifiers are binary alloys of copper with silicon, phosphorus, manganese, magnesium, lithium, or cadmium. The highly oxidized, refined copper melt, containing an appreciable amount of Cu_2O can be cast from the reverberatory or rotary furnace into blister copper shapes and used in the subsequent preparation of fire refined copper. More typically, however, the molten oxidized melt is reduced in the reverberatory or rotary furnace in which it was formed, by using carbon-based reducing agents and then poling. These operations are discussed in detail in the section on refining of high grade copper scrap.

Once a melt meets specifications, principally chemical analysis, the brass or bronze is cast into ingots, cooled, and then packaged for shipping. Refined copper, that has been analyzed and found to meet specification, is either cast into blister copper ingots or is subsequently reduced in the furnace as a continuation of the fire refining operation.

Fumes of metal oxides are produced when the molten metal is blown with air or oxygen to remove metallic impurities, or when green wooden poles are inserted into the bath to reduce the heat. Dust is produced during the charging of fine slags and fine flux materials. The dusts and fumes are controlled through the use of baghouse filters or wet scrubbers. The wet scrubbers on the reverberatory and rotary furnaces are the sole source of wastewater.

REFINING HIGH-GRADE COPPER SCRAP

Black copper produced from smelting of low-grade scrap, slags, drosses, and sludges, and blister copper prepared from intermediate-grade scrap, are eventually brought together with high quality copper scrap (usually No. 2 copper wire, No. 1 heavy copper, No. 2 copper, and light copper) for full fire refining. Full fire refining is required to produce specification copper billets, slabs, cakes, and wire bars. Copper ingots and shot are also produced for making copper base alloys. Fire refined copper may be even further refined by casting the metal into anodes for electrolytic refining. The extent of refining is governed in part by the amount and type of metal impurities and the need for or difficulty of their removal (by fire refining) to meet specifications for the product.

Fire Refining

Fire refining is used to remove excess zinc, lead, iron and tin. Fire refining involves blowing air or oxygen through the molten metal in a reverberatory or rotary furnace. In the production of pure copper products, the blowing is continued until the contained zinc, lead, iron, tin, and other impurities, along with about three percent of the copper, are removed by oxidation. Most of the oxides are trapped in the slag cover. After the contaminated slag is removed, the refined copper is reduced with green wood poles under a charcoal or coke cover. Once the oxygen content meets specifications, the copper is cast into anodes for electrolytic refining or into billets, wire bars, etc. Selected types of flux materials are generally added to assist in the removal of the impurities before poling.

The slags may contain various proportions of the fluxes, silica, iron oxide, phosphorus pentoxide, soda ash, rasorite (a borax type flux), and limestone depending on impurities needed to be removed to obtain the desired composition. Copper-rich slags are reprocessed or sold for that purpose. Copper-poor slags are discarded or sold.

Skimming

After a copper alloy has been refined in a reverberatory or rotary furnace, it is analyzed and adjusted in composition if necessary. The temperature is adjusted and slags are skimmed from the furnace. These slags are generally reprocessed to remove copper values trapped in the slag. The slag may be processed by the smelter or sold to larger smelters for processing.

The slags are either crushed wet or dry and wet screened or tabled to concentrate the copper content, or the entire copper-rich slag may also be charged into a blast furnace or cupola for remelting and separation of the copper from the other ingredients. If the metal content of the slag is 45 percent or above, some facilities will charge the slag directly into a rotary or reverberatory furnace. Wastewater is generated in plants that use wet crushing and concentrating.

Electrolytic Refining

High-purity cathode copper is produced through electrolytic refining. Anode copper, often containing precious metals and impurities such as nickel, are placed into the cells in an alternating fashion with thin copper starter sheets, which after electrolytic deposition become cathodes of refined copper. The electrolytic refining process is shown schematically in Figure III-3 (page 1242).

The cathodes are removed periodically from the electrolytic cells, melted, and cast into fine-shape castings, such as wire bar and billets. Used anodes are removed from the cells, rinsed to remove adhering acid, and remelted into new anodes. If nickel is present in the anodes, the nickel content of the electrolyte, as well as the copper content, will build up and a bleed from the circuit must occur. This bleed is often subjected to electrowinning for copper removal (where a lead cathode is used) and cementation.

The spent electrolyte, depleted in copper content, may be partially evaporated by open or barometric condensers in order to produce nickel sulfate as a by-product. Precious metals are recovered as a slime in the bottom of the electrolytic cells and are usually dried and sold to other facilities for precious metal value recovery.

Postelectrolytic Melting and Refining

Refined copper in the form of cathodes along with No. 1 copper wire scrap are melted in reverberatory furnaces or shaft furnaces and cast into desired product shapes such as cakes, billets, and wire bars, as well as ingots. The melting process in the reverberatory furnace may be followed by a blowing step, skimming of the melt, and then poling, followed by preparation for pouring and casting.

The shaft furnace, which uses natural gas as a fuel and operates on the principle of a cupola furnace, continuously melts cathodes, home scrap, and No. 1 copper wire scrap, with "refining" by poling or charcoal reduction being done in a small reverberatory holding furnace just before casting. The molten copper is continuously cast into billets and cakes. Water is used principally for noncontact cooling in the two types of melting furnaces.

Particulate air emissions from the operation are usually controlled by means of baghouses. Wet air pollution control may also be used to control air emissions. In such cases a wastewater is generated.

CASTING

Molten metal from the smelting operations described above is cast into various shapes suitable for shipping, handling, or use in subsequent operations. Copper-base alloys are usually cast into ingots. Black copper, blister copper, and anode copper are also cast in molds and shapes suited for the specific product. Refined copper is cast into shapes suitable for subsequent fabrication steps, taking the form of billets, cakes, wire bars, wire rod, and ingots, or it may be quenched into shot. Casting operations for the various products are described below.

Brass and Bronze Ingot

The melt, which has been analyzed and found to meet specifications, is adjusted to the proper temperature before pouring. Rotary and reverberatory furnaces containing the molten metal are tapped, and the metal is poured into various ingot filling systems. The metal may pour directly into a moving, automatically controlled mold line, in which one or more molds are filled at once; then the flow shuts off while a new set of molds moves into position on an endless conveyer. In another variation, the metal from the furnace is tapped into a ladle and then moved to a mold line, which may be stationary or movable. Molds are sprayed with a mold wash and then dried thoroughly before the ingot is cast. Automatic devices are often used to sprinkle ground charcoal in the molds or onto the molten metal in the molds to provide a special smooth top on the ingots.

The molds are cooled by a water spray or partial immersion of the mold in a tank of water. Once the molten metal has solidified, the ingots are quenched in a pit from which they are removed by a drag conveyer. After drying, they are packed for shipment.

Generally, only steam is discharged during the operation, and water is recycled after cooling and storage in tanks or ponds. The wastewater is discharged periodically to permit the storage tanks to be cleaned of charcoal and mold wash sludges containing some metals or their oxides.

Black and Blister Copper

Black copper (or cupola melt) produced from blast or cupola furnace operations is usually transported or transferred to a converter or a reverberatory or rotary furnace in the molten state to conserve heating requirements. In some cases where the conversion-oriented operation is backlogged or out of synchronization with black copper production, the black copper might be cast into convenient shapes for later use. These shapes take the form of shot, pigs, sows, or any convenient mold shape available. Crude molds formed in sand are often used to cast pigs, sows, or other shapes. Blister copper production may also be out of phase with subsequent reduction operations due to a furnace failure or plant shutdown. In such cases, the blister copper is cast into almost any available mold shape for subsequent use. These molds may be contact or noncontact cooled with water, or they can be air cooled. In those cases where the blister copper is an end product of the smelter, the molds are made of graphite and are air cooled.

Anodes

Partially fire refined copper, that is to be electrolytically refined to remove impurities that are not removed by fire refining or to recover impurities of value, is cast into anodes. The molten metal from the anode furnace is cast in a circular mold conveying system (known as a casting wheel) or a conveyer. The molds may be cooled indirectly, or spray cooled, or both, after the metal has been cast. Once the molten metal has solidified, it is removed from the mold and quenched in a tank of water. The mold is treated with a mold coating or "wash," commonly synthetic bone ash (calcium phosphate), before receiving the next charge of molten anode copper. Much of the spray water is converted to steam. Wastewater containing residual mold wash and some metal oxide scale is generated.

Refined Copper

Fully fire refined copper and melted cathode copper are cast into various shapes suitable for fabrication end use. These shapes are billets, cakes, slabs, wire bar, wire rod, and ingots. Wire bar and ingots are cast into permanent molds on a casting wheel that is internally cooled with water. Once solidified, the wire bar or ingots are removed from the mold and quenched in tanks. The molds are treated with a mold wash and dried before reuse.

Billets, cakes, and wire rod are usually continuously cast or directly chill cast, and the metal is cooled within dies using noncontact and contact cooling water that is recirculated after passing through cooling towers. Wire-rod casting uses exclusively noncontact cooling water as the cast rod is reduced in diameter through a series of water-cooled rolls.

Copper Shot

Copper for alloying purposes is sometimes produced in the form of shot to facilitate handling and remelting. In some cases, the copper is alloyed with phosphorus to increase hardness. Copper shotting operations consist of pouring the molten refined copper directly into a quench pit. Wastewater is generated when the quench pit is periodically discharged for cleaning, and by wet air pollution control devices operating on gas streams generated by the melting furnace.

PROCESS WASTEWATER SOURCES

The principal sources of wastewater in the secondary copper subcategory are:

1. Residue concentration,
2. Slag granulation,
3. Reverberatory and rotary furnace wet air pollution control,
4. Spent electrolyte,
5. Scrap anode rinse water,
6. Casting contact cooling water, and
7. Casting wet air pollution control.

OTHER WASTEWATER SOURCES

There are other wastewater streams associated with the manufacture of secondary copper. These wastewater streams include but are not limited to stormwater runoff, and maintenance and cleanup water. These waste streams are not considered as a part of this rulemaking. EPA believes that the flows and pollutant loadings associated with these waste streams are insignificant relative to the waste streams selected and are best handled by the appropriate permit authority on a case-by-case basis under authority of Section 402 of the Clean Water Act.

AGE, PRODUCTION, AND PROCESS PROFILE

A distribution of the secondary copper plants in the United States is shown in Figure III-4 (page 1243). Figure III-4 shows that most of the secondary copper plants are located around the Great Lakes and New England states.

Table III-1 (page 1237) shows that the average plant age is 20 to 30 years, and that there are five direct, six indirect, and 20 zero discharge plants in the secondary copper subcategory. Table III-2 (page 1238) summarizes the distribution of secondary copper plants for 1976 production levels. Table III-3 (page 1239) provides a summary of the number of secondary copper plants that generate the various process wastewaters identified previously in this section.

TABLE III-1

INITIAL OPERATING YEAR (RANGE) SUMMARY OF PLANTS IN THE SECONDARY COPPER SUBCATEGORY, BY DISCHARGE TYPE

Type of Plant Discharge	1982 to 1968	1967 to 1958	1957 to 1948	1947 to 1938	1937 to 1928	1927 to 1918	1917 to 1903	Insuff. Data	Total
Direct	2	2	1	0	0	0	0	0	5
Indirect	0	1	1	0	2	2	0	0	6
Zero	0	5	4	3	2	2	1	3	20
TOTAL	2	8	6	3	4	4	1	3	31

TABLE III-2

PRODUCTION RANGES FOR PROCESSING PLANTS OF THE SECONDARY COPPER SUBCATEGORY

Production Ranges for 1976 tons/year)	Number of Plants
0 - 5,000	11
5,001 - 10,000	3
10,001 - 20,000	6
20,001 - 30,000	4
30,001 +	4
No Data Reported in dcp	3
Total Number of Plants in Survey	31

TABLE III-3

PRODUCTION PROCESSES UTILIZED BY THE SECONDARY COPPER SUBCATEGORY

Production Process	Number of Plants with Process	Number of Plants Generating Wastewater*
Residue Concentration	7	7
Slag Granulation	5	5
Reverberatory and Rotary Furnace Air Pollution Control	18	5
Electrolytic Refining	6	6
Casting	29	22
Casting Air Pollution Control**	8	3

---

*Due to in-process flow reduction measures, a plant may generate a wastewater but not discharge it.

**Reverberatory and rotary furnace air pollution control plants are not included in the count for casting air pollution control. An attempt was made to distinguish the reverberatory and rotary furnace wet air pollution control systems and the casting wet air pollution control systems that do not use reverberatory and rotary furnaces for casting.

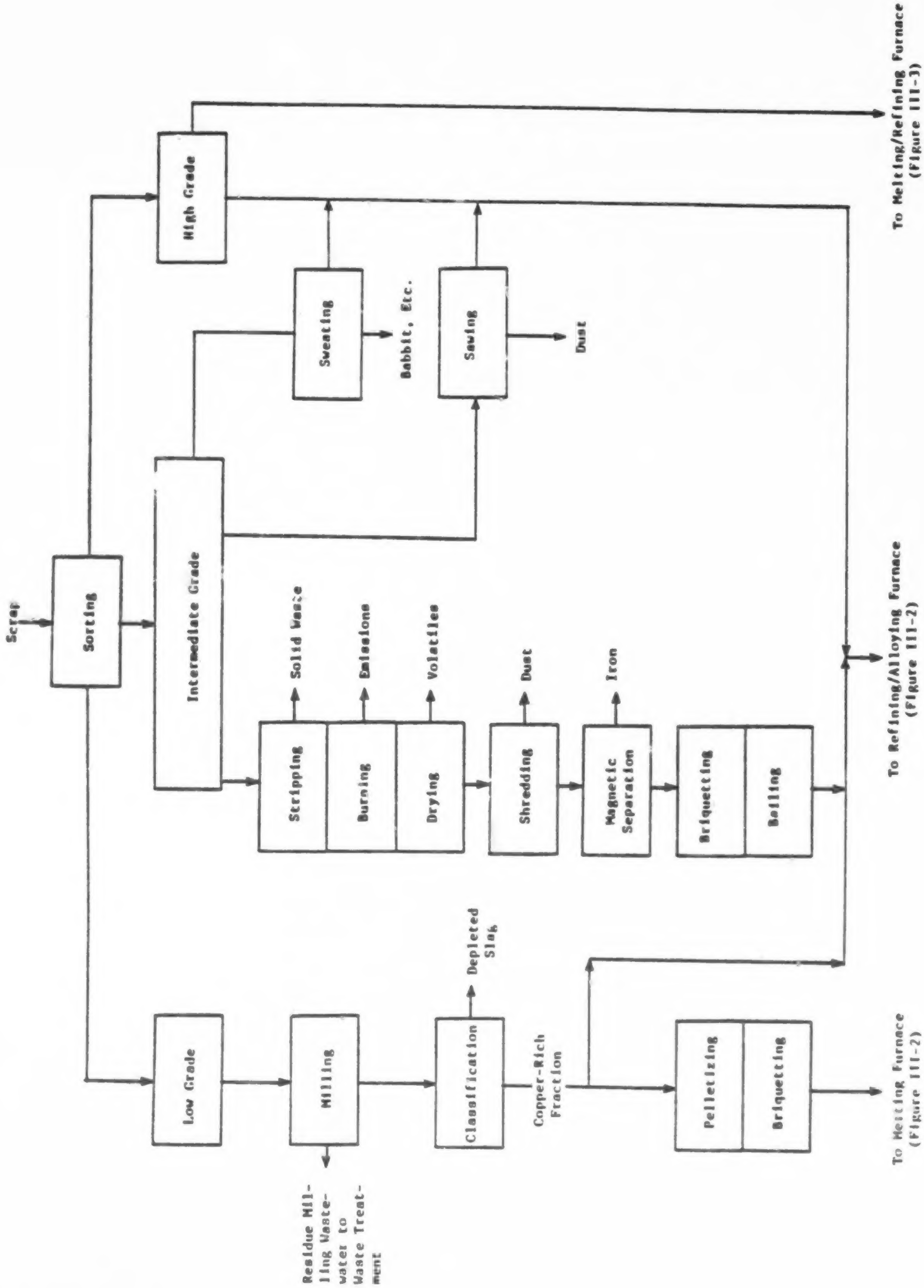
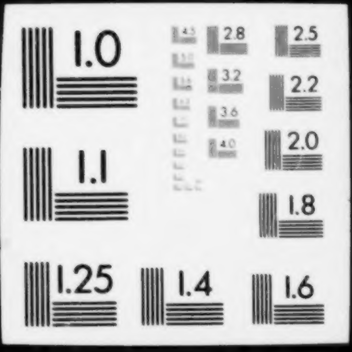

Scrap
Sorting
High Grade
Intermediate Grade
Low Grade
Sweating
Babbit, Etc.
Sawing
Dust
Stripping
Burning
Drying
Solid Waste
Emissions
Volatiles
Shredding
Dust
Magnetic Separation
Iron
Briquetting
Bailing
Milling
Residue Milling Wastewater to Waste Treatment
Classification
Depleted Slag
Copper-Rich Fraction
Pelletizing
Briquetting
To Melting/Refining Furnace (Figure III-3)
To Refining/Alloying Furnace (Figure III-2)
To Melting Furnace (Figure III-2)

Figure III-1

SECONDARY COPPER PRODUCTION PROCESS SCRAP PRETREATMENT

3 OF 5
PB 90
181 983


1.0
4.5
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

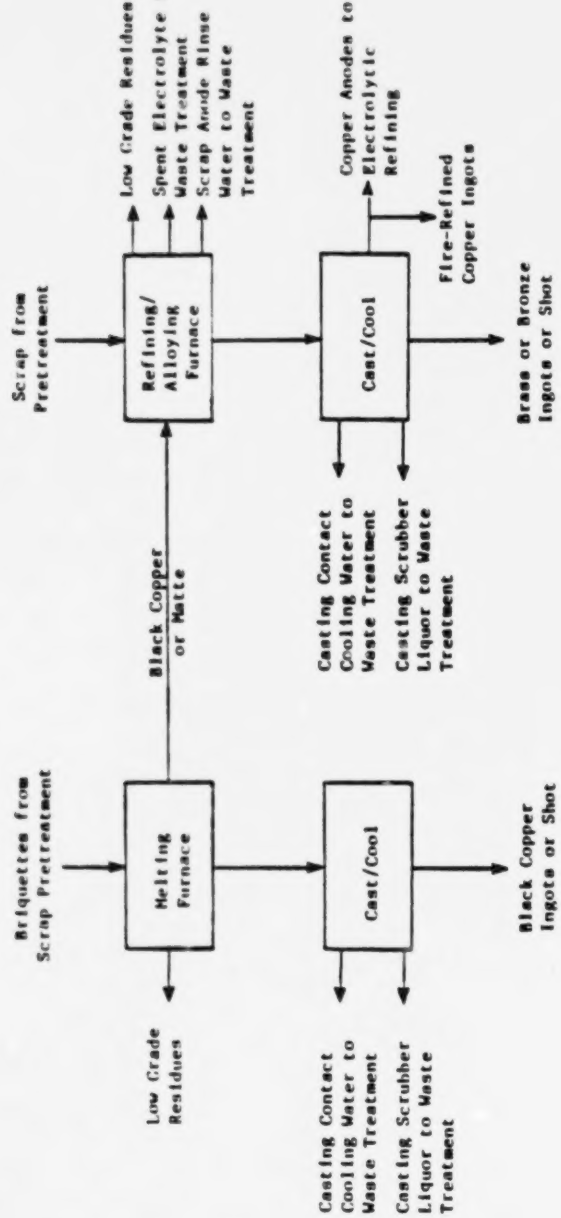

Briquettes from Scrap Pretreatment
Melting Furnace
Low Grade Residues
Cast/Cool
Casting Contact Cooling Water to Waste Treatment
Casting Scrubber Liquor to Waste Treatment
Black Copper Ingots or Shot
Black Copper or Matte
Scrap from Pretreatment
Refining/Alloying Furnace
Low Grade Residues
Spent Electrolyte to Waste Treatment
Scrap Anode Rinse Water to Waste Treatment
Cast/Cool
Casting Contact Cooling Water to Waste Treatment
Casting Scrubber Liquor to Waste Treatment
Brass or Bronze Ingots or Shot
Copper Anodes to Electrolytic Refining
Fire-Refined Copper Ingots

Figure III-2

SECONDARY COPPER PRODUCTION PROCESS SMELTING

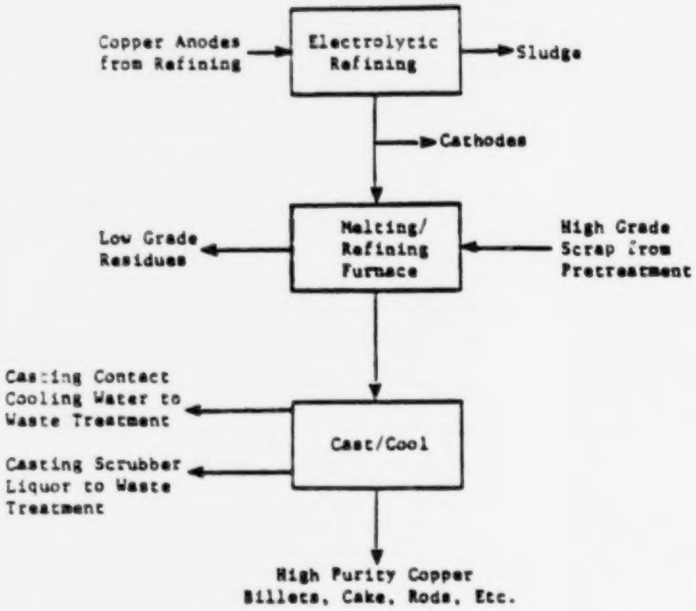

Copper Anodes from Refining
Electrolytic Refining
Sludge
Cathodes
Low Grade Residues
Melting/ Refining Furnace
High Grade Scrap from Pretreatment
Casting Contact Cooling Water to Waste Treatment
Cast/Cool
Casting Scrubber Liquor to Waste Treatment
High Purity Copper Billets, Cake, Rods, Etc.

FIGURE III-3
SECONDARY COPPER PRODUCTION PROCESS ELECTROLYTE REFINING

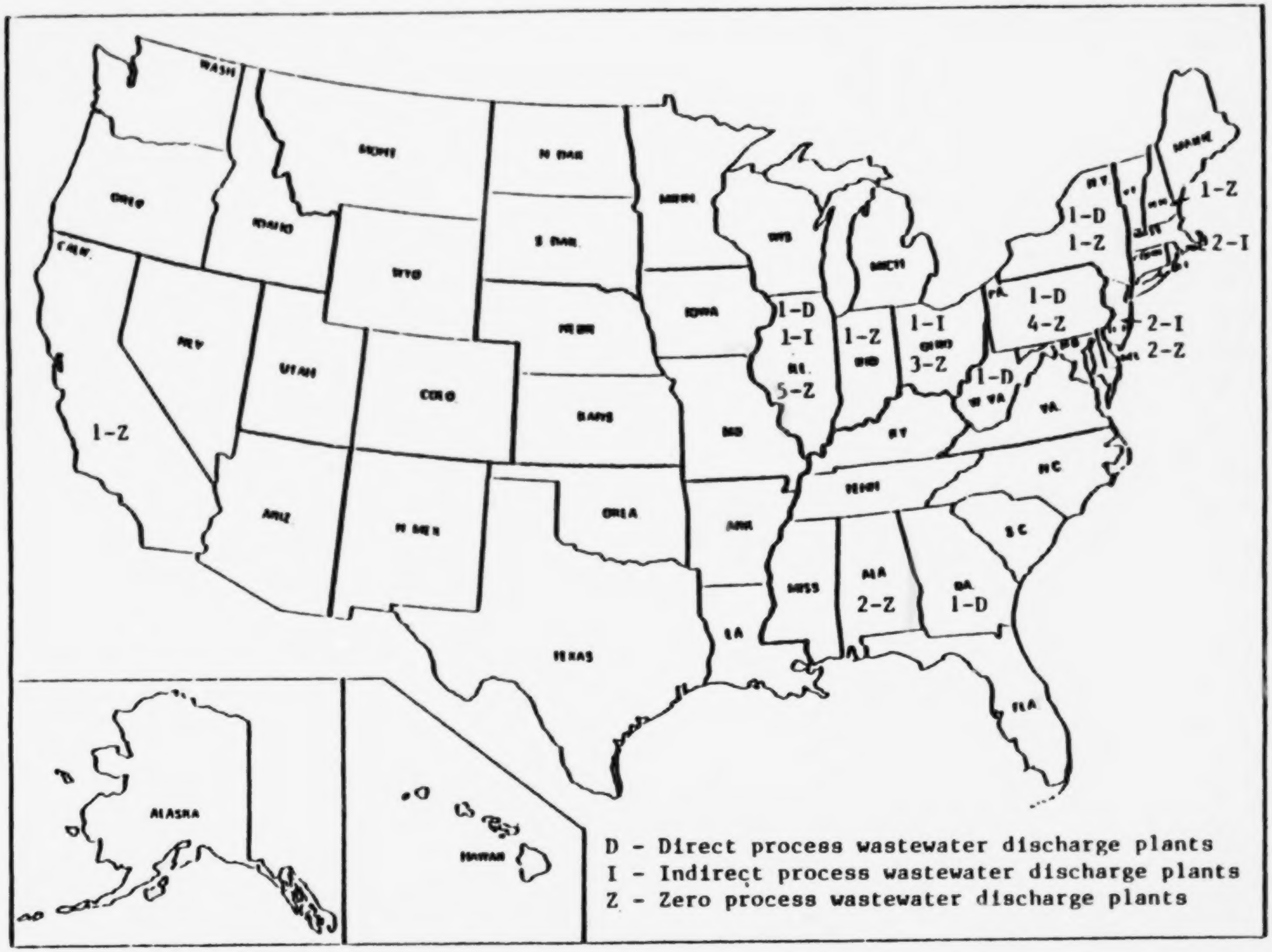

WASH
N DAK
S DAK
WYO
NEV
UTAH
COLO
TEXAS
ALASKA
HAWAII
1-Z
1-D
1-Z
2-I
1-D
4-Z
2-I
2-Z
1-D
W VA
VA.
NC
SC
1-I
OHIO
3-Z
1-Z
IND
1-D
1-I
ILL.
5-Z
KY
MO
ARK
LA
MISS
ALA
2-Z
GA
1-D
FLA
1-Z
D - Direct process wastewater discharge plants
I - Indirect process wastewater discharge plants
Z - Zero process wastewater discharge plants

Figure III-4

GEOGRAPHIC LOCATIONS OF THE SECONDARY COPPER INDUSTRY

SECTION IV

SUBCATEGORIZATION

This section summarizes the factors considered during the designation of the secondary copper subcategory and its related subdivisions.

FACTORS CONSIDERED IN SUBDIVIDING THE SECONDARY COPPER SUBCATEGORY

The general subcategorization factors listed previously were each evaluated when considering subdivision of the secondary copper subcategory. In the discussion the follows, the factors will be discussed as they pertain to this particular subcategory.

The rationale for considering further segmentation of the secondary copper subcategory is based primarily on differences in the production processes and raw materials used. Within this subcategory, a number of different operations are performed, which may or may not have a water use or discharge, and which may require the establishment of separate effluent limitations. While secondary copper is still considered a single subcategory, a more thorough examination of the production processes has illustrated the need for limitations and standards based on a specific set of waste streams. Limitations will be based on specific flow allowances for the following segments or building blocks.

1. Residue concentration,
2. Slag granulation,
3. Reverberatory and rotary furnace wet air pollution control,
4. Spent electrolyte,
5. Scrap anode rinsing,
6. Casting contact cooling, and
7. Casting wet air pollution control.

Two building blocks have been established for wastewater generated in the processing of slags and residues. Slag covers on reverberatory and rotary furnaces are generally raked off before the furnace is tapped. The copper content of the slag can be recovered by melting the slag (along with scrap copper, coke, and fluxes) in a cupola or blast furnace, or by milling and classifying the slag into a waste gangue material and a copper rich concentrate. Wastewater is generated in the concentration of slags or other residues such as drosses, skimming, spills, and sweepings through wet milling and classifying. When slags are melted with scrap copper, coke, and fluxes in blast or cupola furnaces, two products are tapped, a waste or depleted slag, and black copper. The waste slag is granulated in a quench pit or with a high pressure water stream, producing slag granulation wastewater.

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Wet scrubbers are used to remove particulates and metal oxide fumes from reverberatory and rotary furnace off-gases. Therefore, a subdivision for reverberatory and rotary furnace wet air pollution control wastewater is necessary.

A building block has not been established for blast, cupola, or converter furnace wet air pollution control, since no plants in the subcategory use wet air pollution control devices in conjunction with these furnaces.

Two building blocks are established for wastewater associated with electrolytic refining. These subdivisions are established for spent electrolyte wastewaters and scrap anode rinse water. Spent electrolyte is sometimes bled to prevent the build up of copper and nickel in the electrolyte. Depleted anodes are removed from the electrolytic cells and subsequently rinsed with water to remove adhering electrolyte.

Contact cooling water is used for metal cooling at 22 plants. Therefore a casting contact cooling subdivision is necessary. A subdivision has also been established for casting wet air pollution control, since three plants use wet scrubbers to remove fumes and particulates from casting operations.

OTHER FACTORS

The other factors considered in this evaluation were shown to be inappropriate bases for further segmentation. Air pollution control methods, treatment costs, and total energy requirements are functions of the selected subcategorization factors--metal product, raw materials, and production processes. Therefore, they are not independent factors and do affect the segmentation presented. Certain other factors, such as plant age, plant size, and the number of employees, were also evaluated and determined to be inappropriate as the bases for segmentation of secondary copper plants.

PRODUCTION NORMALIZING PARAMETERS

The effluent limitations and standards developed in this document establish mass limitations on the discharge of specific pollutant parameters. To allow these regulations to be applied to plants with various production capacities, the mass of pollutant discharged must be related to a unit of production. This factor is known as the production normalizing parameter (PNP).

The PNPs for the seven segments or building blocks in the secondary copper subcategory are shown in Table IV-1 page 1247).

TABLE IV-1

BUILDING BLOCKS AND PRODUCTION NORMALIZING PARAMETERS IN THE SECONDARY COPPER SUBCATEGORY

	Building block	PNP
1.	Residue concentration	kkg of slag or residue processed
2.	Slag granulation	kkg of blast and cupola furnace copper produced
3.	Reverberatory and furnace wet air pollution control	kkg of reverberatory and rotary furnace copper produced
4.	Spent electrolyte	kkg of cathode copper produced
5.	Scrap and rinse water	kkg of cathode copper produced
6.	Casting contact cooling	kkg of copper cast
7.	Casting wet air pollution control	kkg of copper cast

SECTION V

WATER USE AND WASTEWATER CHARACTERISTICS

This section describes the characteristics of wastewater associated with the secondary copper subcategory. Data used to quantify wastewater flow and pollutant concentrations are presented, summarized, and discussed. The contribution of specific production processes to the overall wastewater discharge from secondary copper plants is identified whenever possible.

The two principal data sources used in the development of effluent limitations and standards for this subcategory are data collection portfolios and field sampling results. Data collection portfolios, completed for the secondary copper subcategory, contain information regarding wastewater flows and production levels.

In order to quantify the pollutant discharge from secondary copper plants, a field sampling program was conducted. Wastewater samples were collected in two phases: screening and verification. The first phase, screen sampling, was to identify which toxic pollutants were present in the wastewaters from production of the various metals. Screening samples were analyzed for 125 of the 126 toxic pollutants and other pollutants deemed appropriate. Because the analytical standard for TCDD was judged to be too hazardous to be made generally available, samples were never analyzed for this pollutant. There is no reason to expect that TCDD would be present in secondary copper wastewater. A total of 10 plants were selected for screen sampling in the nonferrous metals manufacturing category. A complete list of the pollutants considered and a summary of the techniques used in sampling and laboratory analyses are included in Section V of Vol. 1. In general, the samples were analyzed for three classes of pollutants: toxic organic pollutants, toxic metal pollutants, and criteria pollutants (which includes both conventional and nonconventional pollutants).

As described in Section IV of this supplement, the secondary copper subcategory has been further segmented into seven building blocks. As such, the promulgated regulation contains mass discharge limitations and standards for seven unit processes discharging process wastewaters. Differences in the wastewater characteristics associated with these building blocks are to be expected. For this reason, wastewater streams corresponding to each segment are addressed separately in the discussions that follow.

WASTEWATER SOURCES, DISCHARGE RATES, AND CHARACTERISTICS

The wastewater data presented in this section were evaluated in light of production process information compiled during this study. As a result, it was possible to identify the principal wastewater sources in the secondary copper subcategory. These include:

1. Residue concentration,
2. Slag granulation,
3. Reverberatory and rotary furnace wet air pollution control,
4. Spent electrolyte,
5. Scrap anode rinsing,
6. Casting contact cooling, and
7. Casting wet air pollution control.

Data supplied by dcp responses were used to calculate the amount of water used and discharged per metric ton of production. The two ratios calculated are differentiated by the flow rate used in the calculation. Water use is defined as the volume of water or other fluid (e.g., electrolyte) required for a given process per mass of copper product and is therefore based on the sum of recycle and make-up flows to a given process. Wastewater flow discharged after pretreatment or recycle (if these are present) is used in calculating the production normalized flow--the volume of wastewater discharged from a given process to further treatment, disposal, or discharge per mass of copper produced. Differences between the water use and wastewater flows associated with a given stream result from recycle, evaporation, and carry over on the product. The production values used in calculations correspond to the production normalizing parameter, PNP, assigned to each stream, as outlined in Section IV. The production normalized flows were compiled and statistically analyzed by stream type. Where appropriate, an attempt was made to identify factors that could account for variations in water use. This information is summarized in this section. As an example, scrap anode rinse wastewater flow is related to the cathode copper production. As such, the discharge rate is expressed in liters of rinse waste water per metric ton of cathode copper production (gallons of rinse water per ton of cathode copper production).

Characteristics of wastewater from the previously listed processes were determined from sampling data collected at secondary copper plants. This data was used in two ways. Pollutants were selected for regulation based on the data and the sampling data was also used to estimate the yearly mass of pollutant generated by each waste stream for the entire subcategory. There were a total of five site visits, which represents 11 percent of the secondary copper subcategory. Diagrams indicating the sampling sites and contributing production processes are shown in Figures V-1 to V-5 (pages 1285 - 1289)

In the data collection portfolios, plants were asked to indicate whether or not any of the toxic pollutants were believed to be present in their wastewater. The responses for the toxic metals are summarized in Table V-1 (page 1256).

All plants responding to the portion of the dcp concerning the presence of the toxic organic pollutants indicated that they all were either known or believed to be absent with the exception of fluorene. Two plants reported that fluorene was known to be present while one plant reported that fluorene was believed to be present. However, as reported in Section VI, fluorene was not detected in 12 samples from five waste streams collected during the Agency's sampling and analysis program.

The raw wastewater sampling data for the secondary copper subcategory are presented in Tables V-9 through V-13 (pages 1264 - 1274). Treated wastewater sampling data are shown in Tables V-14 through V-17 (pages 1279 - 1283). The stream codes displayed in Tables V-8 through V-16 may be used to identify the location of each of the samples on the process flow diagrams in Figures V-1 through V-5. Where no data are listed for a specific day of sampling, the wastewater samples for the stream were not collected. If the analyses did not detect a pollutant in a waste stream, the pollutant was omitted from the table.

The data tables included some samples measured at concentrations considered not quantifiable. The base neutral extractable, acid extractable, and volatile toxic organics generally are considered not quantifiable at concentrations equal to or less than 0.010 mg/l. Below this concentration, organic analytical results are not quantitatively accurate; however, the analyses are useful to indicate the presence of a particular pollutant. The pesticide fraction is considered not quantifiable at concentrations equal to or less than 0.005 mg/l. Nonquantifiable results are designated in the tables with an asterisk (double asterisk for pesticides).

These detection limits shown on the data tables are not the same in all cases as the published detection limits for these pollutants by the same analytical methods. The detection limits used were reported with the analytical data and hence are the appropriate limits to apply to the data. Detection limit variation can occur as a result of a number of laboratory-specific, equipment-specific, and daily operator-specific factors. These factors can include day-to-day differences in machine calibration, variation in stock solutions, and variation in operators.

The statistical analysis of data includes some samples measured at concentrations considered not quantifiable. Data reported as an asterisk are considered as detected but below quantifiable concentrations, and a value of zero is used for averaging. Toxic organic, nonconventional, and conventional pollutant data reported with a "less than" sign are considered as detected but not further quantifiable. A value of zero is also used for averaging. If a pollutant is reported as not detected, it is excluded in calculating the average. Finally, toxic metal values reported as less than a certain value were considered as not detected and a value of zero is used in the calculation of the average. For example, three samples reported as ND, *, and 0.021

mg/l have an average value of 0.010 mg/l. The averages calculated are presented with the sampling data. These values were not used in the selection of pollutant parameters.

In the following discussion, water use and field sampling data are presented for each operation. Appropriate tubing or background blank and source water concentrations are presented with the summaries of the sampling data. Figures V-1 through V-5 (pages 1285 - 1289) show the location of wastewater sampling sites at each facility. The method by which each sample was collected is indicated by number, as follows:

1	one-time grab
2	24-hour manual composite
3	24-hour automatic composite
4	48-hour manual composite
5	48-hour automatic composite
6	72-hour manual composite
7	72-hour automatic composite

SECONDARY COPPER WASTEWATER SOURCES AND CHARACTERISTICS

Presented below is a discussion of the characteristics of the significant wastewater sources attributable to the processing of secondary copper.

Residue Concentration

The copper content can be concentrated in slags and other residues, such as drosses, skimmings, spills, and sweepings, before charging the concentrates into rotary or reverberatory furnaces. The residues are sometimes concentrated by wet milling and classifying, producing a residue concentration waste stream. The water use and discharge rates for residue concentration in liters of water per metric ton of slag or residue processed are shown in Table V-2 (page 1257).

Raw wastewater data for residue concentration are presented in Table V-9 (page 1264). This waste stream is characterized by treatable concentrations of dissolved toxic metal pollutants and suspended solids. The toxic metals are soluble components of the slags and residues, and the suspended solids are from milling fines entrained in the water.

Slag Granulation

Five plants report the use of water for blast or cupola furnace slag granulation. This wastewater is generated when slag is granulated with high pressure water jets, or in quench pits prior to disposal. The water use and discharge rates for slag granulation in liters of water per metric ton of blast or cupola furnace production are shown in Table V-3 (page 1258).

The Agency did not collect any raw wastewater sampling data from slag granulation operations at secondary copper plants. However, the characteristics of this wastewater are generally comparable to those of residue concentration wastewater, since materials from nearly identical sources are being treated in either case. Thus, slag granulation wastewater contains treatable concentrations of dissolved toxic metal pollutants and suspended solids.

Reverberatory and Rotary Furnace Wet Air Pollution Control

Five plants report the use of wet air pollution control devices to contain metal oxide fumes and dust from reverberatory and rotary furnace operations. Fumes of metal oxides are produced when the molten metal is blown with air or oxygen to remove metallic impurities, or when green wooden poles are inserted into the bath to deoxidize the heat. Dust will be produced during the charging of fine slags or fine flux materials. When wet air pollution control is used, the metal oxides and dust will be contained in the water as suspended solids and dissolved toxic metals. Raw wastewater data for reverberatory and rotary furnace wet air pollution control are shown in Table V-10 (page 1268). As expected, toxic metal pollutants and suspended solids are present in treat- able concentrations. Table V-10 also shows that this wastewater is acidic (pH of 1.6 to 2.5).

The water use and discharge rates for reverberatory and rotary furnace wet air pollution control are presented in Table V-4 page 1259).

Spent Electrolyte

Normally, electrolyte is continuously circulated through thickeners and filters to remove solids, and recycled back through the electrolytic cells. It is necessary to blowdown a fraction of the electrolyte to prevent the build-up of copper and nickel. This slip stream is treated to recover nickel and copper, and recycled or discharged. Table V-5 (page 1260) presents the electrolyte use and discharge rates for spent electrolyte in liters per metric ton of cathode copper produced.

Raw wastewater sampling data for spent electrolyte are shown in Table V-11 (page 1270). This waste stream is characterized by treatable concentrations of toxic metal pollutants (particularly copper, lead, and zinc) and suspended solids. The pH of the spent electrolyte in the wastewater samples ranged from 1.48 to 3.45.

Scrap Anode Rinsing

Anodes removed from electrolytic cells are sometimes rinsed before further processing. As shown in Table V-6 (page 1261), only two plants reported the use of rinse water for scrap anode cleaning, and both of those plants practice 100 percent recycle of the rinse water. The Agency did not collect any raw wastewater samples from anode rinsing operations. Wastewater from this operation should contain treatable concentrations of total suspended solids and dissolved toxic metal pollutants, which are a result of impurities in the modes that are released into the rinse water.

Casting Contact Cooling

Twenty-two plants report the use of contact cooling water to cool molten metal cast into ingots, shot, and anodes. Anodes and rough brass or bronze ingots are generally water spray-cooled to rapidly solidify the casting, and the casting is then quenched in a tank of water. Smooth brass or bronze ingots must be slowly cooled in the mold under a layer of charcoal to produce the smooth surface requested by certain customers. Ingot mold lines are quite long for the production of smooth ingots. The ingots are permitted to air cool in the mold during the first portion of the conveyer travel, the bottom of the ingot mold is submerged in a tank of water during the second portion of the conveyer travel, and finally the solidified ingot is discharged into a quenching tank of water. Part of the charcoal burns during the ingots' travel period on the conveyer. The unburned charcoal and charcoal ash all go into the ingot cooling water. These residues settle as a sludge and are periodically cleaned out of the quenching tanks and subsequent settling tanks or ponds. The water may or may not be recycled. In addition to the charcoal and charcoal ash, the wastewater pollutants associated with contact cooling are metal oxides from the ingot surface, refractory mold wash (calcium phosphate), and flour dust. Charcoal is not used when casting copper anodes, but the mold wash is used and the wash ends up in the contact cooling water. The raw waste water data for casting contact cooling water is presented in Table V-12 (page 1272). Copper, lead, zinc, and total suspended solids are all present in treatable concentrations.

The water use and discharge rates for casting contact cooling in liters of water per metric ton of copper cast are shown in Table V-7 (page 1262).

Casting Wet Air Pollution Control

Wet air pollution control devices are used to control fumes produced from casting operations at three plants. Two of these plants use scrubbers to contain fumes produced from alloying copper with phosphor in induction furnaces. The third plant did not report why it uses a scrubber for casting, however, this plant casts brass and bronze ingots which produce metal oxide fumes when poured. These fumes can be controlled by a scrubber.

The water use and discharge rates for casting wet air pollution control in liters of water per metric ton of copper cast are shown in Table V-8 (page 1263).

Raw wastewater samples were not collected for this stream. However, since both casting, and reverberatory and rotary furnace water pollution control devices control metal oxide fumes, their wastewaters will be similar. Therefore, casting wet air pollution wastewater contains toxic metal pollutants and suspended solids.

TABLE V-1

TOXIC METALS BELIEVED TO BE PRESENT IN SECONDARY COPPER WASTEWATER DCP DATA

Toxic Metal	Known Present	Believed Present	Believed Absent	Known Absent
Antimony	2	1	7	-
Arsenic	1	-	8	1
Beryllium	1	-	9	-
Cadmium	3	-	7	-
Chromium	2	1	7	-
Copper	7	1	2	-
Lead	6	1	3	-
Mercury	2	1	6	1
Nickel	4	1	5	-
Selenium	-	-	9	1
Silver	1	1	8	-
Zinc	7	1	1	-

TABLE V-2

WATER USE AND DISCHARGE RATES FOR RESIDUE CONCENTRATION

(l/kkg of slag or residue processed)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
15	0	6,702	6,702
23	100	NR	0
49	100	6,680	0
50	100	NR	0
55	100	NR	0
220	NR	NR	677
4507	100	NR	0

NR - Present, but data not reported in dcp.

TABLE V-3

WATER USE AND DISCHARGE RATES FOR SLAG GRANULATION

(l/kkg of blast and cupola furnace production)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
26*	NR	NR	0
35	100	NR	0
36	100	17,210	0
49	100	40,900	0
62	100	65,800	0

*Wastewater is evaporated.

NR - Present, but data not reported in dcp.

TABLE V-4

WATER USE AND DISCHARGE RATES FOR REVERBERATORY AND ROTARY FURNACE WET AIR POLLUTION CONTROL

(l/kkg of reverberatory and rotary furnace copper produced)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
22	100	274,200	0
46	0	7,226	7,226
50	100	NR	0
52	100	NR	0
207	81	25,000	4,695

NR - Present, but data not reported in dcp.

TABLE V-5

ELECTROLYTE USE AND DISCHARGE RATES

(l/kkg of cathode copper produced)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
22*	0	263.2	263.2
62	100	NR	0
78*	NR	NR	1,499
207	NR	NR	1,124

*Spent electrolyte is contract hauled.

NR - Present, but data not reported in dcp.

TABLE V-6

WATER USE AND DISCHARGE RATES FOR SCRAP ANODE RINSING

(1/kkg of cathode copper produced)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
78	100	NR	0
670	100	NR	0

NR - Present, but data not reported in dcp.

TABLE V-7

WATER USE AND DISCHARGE RATES FOR CASTING CONTACT COOLING

(l/kkg of copper cast)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
15	0	148	148
16	0	925	925
17	0	1.45	1.45
18	100	NR	0
21	100	NR	0
22	0	21,586	21,586
23	100	NR	0
26	100	NR	0
35	100	NR	0
36	100	14,720	0
37	NR	NR	1,406
49	100	6,070	0
50	NR	NR	NR
52	100	NR	0
55	100	NR	0
58*	0	109	109
62	100	NR	0
207	0	12,614	12,614
220	99	23,700	237
662	0	4,100	4,100
4508	0	917	917
9050	0	109	109

*Contact cooling water is dry well injected.

NR - Present, but data not reported in dcp.

TABLE V-7

WATER USE AND DISCHARGE RATES FOR CASTING WET AIR POLLUTION CONTROL

(l/kkg of copper cast)

Plant Code	Percent Recycle	Production Normalized Water Use	Production Normalized Discharge Flow
36	100	NR	0
37	NR	NR	281
78	0	337	337

NR - Present, but data not reported in dcp.

TABLE V-9

SECONDARY COPPER SAMPLING DATA
RESIDUE CONCENTRATION
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
10. 1,2-dichloroethane	2	3		0.022		ND	0.022
23. chloroform	2	3		0.26		0.052	0.156
29. 1,1-dichloroethylene	2	3		0.667		ND	0.667
30. 1,2-trans-dichloro-ethylene	2	3		ND		0.012	0.012
44. methylene chloride	2	3		0.58		ND	0.58
66. bis(2-ethylhexyl) phthalate	2	3			1	0.06	0.53
	104	2	0.144	0.054			0.054
68. di-n-butyl phthalate	2	3			0.4	0.024	0.212
	104	2	*	0.012			0.012
86. toluene	2	3		0.015		ND	0.015
87. trichloroethylene	2	3		0.023		0.058	0.040
109. PCB-1232 (b) 110. PCB-1248 (b) 111. PCB-1260 (b) 112. PCB-1016 (b)	2	3		<0.007			<0.007
	104	2	**	**			**

TABLE V-9 (Continued)

SECONDARY COPPER SAMPLING DATA
RESIDUE CONCENTRATION
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
114. antimony	2	3	<0.1	0.013	0.3	0.35	0.22
	104	2		<0.1			<0.1
115. arsenic	2	3	<0.01	0.067	0.175	1	0.414
	104	2		0.11			0.11
117. beryllium	2	3	<0.001	0.16	0.17	0.16	0.16
	104	2		0.1			0.1
118. cadmium	2	3	0.03	0.8	0.8	0.4	0.7
	104	2		0.08			0.08
119. chromium	2	3	<0.005	0.24	<0.24	<0.24	<0.08
	104	2		0.7			0.7
120. copper	2	3	<0.006	90	100	100	97
	104	2		40			40
122. lead	2	3	<0.02	40	20	60	40
	104	2		10			10
123. mercury	2	3	0.0001	0.0004	0.0007	0.005	0.0005
	104	2		0.0007			0.0007
124. nickel	2	3	<0.005	2	2	2	2
	104	2		3			3

TABLE V-9 (Continued)

SECONDARY COPPER SAMPLING DATA
RESIDUE CONCENTRATION
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
125. selenium	2	3		0.005	0.5	0.3	0.268
	104	2	<0.01	<0.01			<0.01
128. zinc	2	3		300	300		300
	104	2	<0.06	40			40
Nonconventionals							
chemical oxygen demand (COD)	2	3		317	1,030		674
	104	2		122			122
total organic carbon (TOC)	2	3		82	189		136
	104	2		22			22
phenols (total; by 4-AAP method)	2	1		0.272	0.313		0.293
Conventionals							
oil and grease	2	1		20	180		100
total suspended solids (TSS)	2	3		7,660	8,790		8,230
	104	2		2,348			2,348
pH (standard units)	2	1		6.0	7.0	7.0	

TABLE V-9 (Continued)

SECONDARY COPPER SAMPLING DATA
RESIDUE CONCENTRATION
RAW WASTEWATER

(a) No samples were analyzed for the acid extractable toxic organic priority pollutants.

(b) Reported together.

Sample Type: Note: These numbers also apply to subsequent data tables.

1 - one-time grab
2 - 24-hour manual composite
3 - 24-hour automatic composite
4 - 48-hour manual composite
5 - 48-hour automatic composite
6 - 72-hour manual composite
7 - 72-hour automatic composite

*Less than or equal to 0.01 mg/l.

**Less than or equal to 0.005 mg/l.

TABLE V-10

SECONDARY COPPER SAMPLING DATA
WET AIR POLLUTION CONTROL
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
6. carbon tetrachloride	58	1		ND	0.116	ND	0.116
23. chloroform	58	1	0.011	0.026	0.11	0.113	0.083
66. bis(2-ethylhexyl) phthalate	58	3	0.1650	0.1760	0.2290	*	0.1350
68. di-n-butyl phthalate	58	3	*	*	0.026	ND	0.013
69. di-n-octyl phthalate	58	3		ND	0.067	ND	0.067
78. anthracene (a) 81. phenanthrene (a)	58	3		ND	<0.012	ND	<0.012
118. cadmium	58	3	<0.002	<0.02	<0.002	<0.002	<0.008
119. chromium	58	3	<0.005	0.4	0.03	0.01	0.15
120. copper	58	3	0.2	30	7	8	15
122. lead	58	3	<0.02	0.9	0.2	0.3	0.5
123. mercury	58	3	0.0001	0.0002	0.0006	0.0001	0.0003
124. nickel	58	3	<0.005	20	0.8	0.1	7.0
126. silver	58	3	<0.02	<0.08	<0.02	<0.02	<0.04
128. zinc	58	3	<0.06	3	0.7	0.7	1.5
Nonconventionals							
chemical oxygen demand (COD)	58	3	<5	14	73	21	36
phenols (total; by 4-AAP method)	58	2		0.004	0.008	0.007	0.006
total organic carbon (TOC)	58	3	5	4	105	20	43

TABLE V-10 (Continued)

SECONDARY COPPER SAMPLING DATA
WET AIR POLLUTION CONTROL
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Conventionals							
oil and grease	58	1		7	2	5	5
total suspended solids (TSS)	58	3	7	6	3	3	4
pH (standard units)	58	1		2.0	1.6	2.5	

(a) Reported together.

TABLE V-11

SECONDARY COPPER SAMPLING DATA
SPENT ELECTROLYTE
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
1. acenaphthene	19	3		0.019	0.036	ND	0.028
4. benzene	19	2		<0.27	0.019	<0.043	<0.006
10. 1,2-dichloroethane	19	2		ND	0.06	*	0.03
23. chloroform	19	2		0.077	1.19	0.124	0.464
25. 1,2-dichlorobenzene (b)	19	3		ND	0.117	0.113	0.115
26. 1,3-dichlorobenzene (b)							
27. 1,4-dichlorobenzene (b)							
29. 1,1-dichloroethylene	19	2		ND	0.038	ND	0.038
30. 1,2-trans-di-chloroethylene	19	2		0.157	ND	0.028	0.093
39. fluoranthene	19	3		ND	0.069	0.258	0.164
44. methylene chloride	19	2		ND	0.64	ND	0.64
55. naphthalene	19	3		0.042	5.0	1.6	2.214
66. bis(2-ethylhexyl) phthalate	19	3		ND	0.1	0.175	0.138
67. butyl benzyl phthalate	19	3		0.056	ND	ND	0.056
68. di-n-butyl phthalate	19	3		0.039	0.083	ND	0.075
70. diethyl phthalate	19	3		0.042	0.083	ND	0.063
76. chrysene	19	3		ND	0.056	ND	0.056
77. acenaphthylene	19	3		0.042	0.117	0.113	0.091
78. anthracene (c)	19	3		ND	ND	0.1	0.1
81. phenanthrene (c)							
84. pyrene	19	3		ND	0.158	0.204	0.182
85. tetrachloroethylene	19	2		*	0.072	*	0.024

TABLE V-11 (Continued)

SECONDARY COPPER SAMPLING DATA
SPENT ELECTROLYTE
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
86. toluene	19	2		ND	0.015	ND	0.015
87. trichloroethylene	19	2		<0.716	0.106	0.121	<0.076
117. beryllium	19	3		0.05	<0.02	<0.02	<0.02
118. cadmium	19	3		2.0	0.9	0.6	1.2
119. chromium	19	3		5	2	0.39	2.13
120. copper	19	3		3,630	1,900	900	2,140
121. cyanide	19	3		0.005	0.002	0.005	0.004
122. lead	19	3		30	20	10	20
123. mercury	19	3		0.0007	0.0004	0.0005	0.0053
124. nickel	19	3		530	270	130	310
128. zinc	19	3		170	80	40	97
Nonconventionals							
chemical oxygen demand (COD)	19	3		95	76	53	75
fluoride	19	3		0.19	0.47	0.2	0.29
phenols (total; by 4-AAP method)	19	1		0.027	0.141	0.073	0.803
total organic carbon (TOC)	19	3		40	28	22	30
Conventionals							
oil and grease	19	1		3	2	6	4
total suspended solids (TSS)	19	3		84	68	43	65
pH (standards units)	19	1		1.48	3.45	2	

(a) No samples were analyzed for the acid extractable toxic organic pollutants. Three samples were analyzed for the pesticide fraction; none was detected above its analytical quantification concentration.

(b),(c) Reported together.

TABLE V-12

SECONDARY COPPER SAMPLING DATA
CASTING CONTACT COOLING
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
15. 1,1,2,2-tetrachloroethane	121	2	*	ND	*	*	*
23. chloroform	121	2	0.043		0.019	0.02	0.020
39. fluoranthene	121	2	ND	*	*	*	*
66. bis(2-ethylhexyl) phthalate	121	2	*	0.041	0.023	0.019	0.028
67. butyl benzyl phthalate	121	2	*	0.011	*	*	0.004
68. di-n-butyl phthalate	121	2	*	0.021	*	*	0.007
69. di-n-octyl phthalate	121	2	*	*	*	*	*
70. diethyl phthalate	121	2	ND	*	*	ND	*
71. dimthyl phthalate	121	2	ND	*	*	*	*
74. 3,4-benzofluoranthene (a)							
75. benzo(k)fluoranthene (a)	121	2	ND	ND	*	ND	*
76. chrysene	121	2	*	ND	*	ND	*
78. anthracene (b)							
81. phenanthrene (b)	121	2	ND	*	*	*	*
84. pyrene	121	2	*	*	*	*	*
85. tetrachloroethylene	121	2	*		*	*	*
115. arsenic	121	2	0.01	0.01	0.01	0.01	0.01
117. beryllium	121	2	0.001	0.001	0.001	0.001	0.001
118. cadmium	121	2	0.002	0.006	0.009	0.006	0.007
119. chromium	121	2	0.008	0.008	0.01	0.02	0.013
120. copper	121	2	0.008	0.3	1	0.6	0.6
1--. cyanide	121	2		0.001	0.001	0.001	0.001
122. lead	121	2	0.02	1	4	3	3

TABLE V-12 (Continued)

SECONDARY COPPER SAMPLING DATA
CASTING CONTACT COOLING
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
123. mercury	121	2	0.0001	0.0001	0.0001	0.0001	0.0001
124. nickel	121	2	0.005	0.007	0.02	0.01	0.012
125. selenium	121	2	0.01	0.01	0.01	0.01	0.01
126. silver	121	2	0.02	0.02	0.02	0.02	0.02
128. zinc	121	2	0.06	2	5	3	3
Nonconventionals							
chemical oxygen demand (COD)	121	2		10	8	11	10
phenols (total; by 4-AAP	121	2		0.008	0.008	0.012	0.009
total organic carbon (TOC)	121	2		1	1	1	1
Conventionals							
oil and grease	121	2			3	2	3
total suspended solids (TSS)	121	2		22	8	8	13

(a),(b) Reported together.

TABLE V-13

SECONDARY COPPER SAMPLING DATA
MISCELLANEOUS RAW WASTEWATER
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted)			
				Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
4. benzene	1	3		*	0.016	<0.02	<0.005
	102	1	*	ND	ND	ND	
6. carbon tetrachloride	1	3		ND	0.011	ND	0.011
	102	1	ND	ND	ND	ND	
9. hexachloroethane	1	3			5.0	ND	5.0
	102	3	ND	ND	ND	ND	
10. 1,2-dichloroethane	1	3		0.014	ND	ND	0.014
	102	1	ND	ND	ND	ND	
23. chloroform	1	3		0.219	0.074	*	0.098
	102	1	*	0.016	0.012	0.04	0.023
29. 1,1-dichloroethylene	1	3		0.176	ND	ND	0.176
	102	1	ND	ND	ND	ND	
30. 1,2-trans-di-chloro-ethylene	1	3		ND	*	ND	*
	102	1	0.013	ND	ND	*	*
39. fluoranthene	1	3			3	ND	3
	102	3	*	ND			
44. methylene chloride	1	3		0.8	ND	ND	0.8
	102	1	ND	ND	ND	ND	

TABLE V-13 (Continued)

SECONDARY COPPER SAMPLING DATA
MISCELLANEOUS RAW WASTEWATER
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
55. naphthalene	1	3			*	ND	*
	102	3	ND	ND			
60. 4,6-dinitro-o-cresol	1	3			0.0125	ND	0.0125
65. phenol	1	3			0.043	ND	0.043
66. bis(2-ethylhexyl) phthalate	1	3			7	0.015	3.508
	102	3	0.144	4.4			4.4
68. di-n-butyl phthalate	1	3			ND	*	*
	102	3	*	*			*
76. chrysene	1	3			10	ND	10
	102	3	ND	ND			
78. anthracene (a)	1	3		<6	ND	0.00	<6.00
	102	3	ND	ND			
84. pyrene	1	3			7	ND	7
	102	3	ND	ND			
85. tetrachloroethylene	1	3		0.054	<0.03	ND	<0.027
	102	1	*	*	*	*	*
86. toluene	1	3		0.025	ND	ND	0.025
	102	1	ND	ND	ND	ND	
87. trichloroethylene	1	3		0.039	0.091	0.1	0.077
	102	1	<0.038	ND	ND	ND	

TABLE V-13 (Continued)

SECONDARY COPPER SAMPLING DATA
MISCELLANEOUS RAW WASTEWATER
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
106. PCB-1242 (b)							
107. PCB-1254 (b)	1	3		<0.009			<0.009
108. PCB-1221 (b)	102	3	**	**			**
109. PCB-1232 (c)							
110. PCB-1248 (c)	1	3		<0.011			<0.011
111. PCB-1260 (c)	102	3	**	**			**
112. PCB-1016 (c)							
114. antimony	1	3		0.011	2.0	0.012	0.674
	102	3	<0.1	<0.1			<0.1
115. arsenic	1	3		0.002	1.0	<0.002	<0.334
	102	3	<0.01	0.15			0.15
117. beryllium	1	3		<0.02	0.63	0.1	<0.25
	102	3	<0.001	<0.001			<0.001
118. cadmium	1	3		12.7	<0.2	10	<7.6
	102	3	0.03	2			2
119. chromium	1	3		<0.24	60	0.56	<20.27
	102	3	<0.005	0.01			0.01
120. copper	1	3		50.1	3	200	84.4
	102	3	<0.006	20			20
121. cyanide	1	3		0.001	0.028		0.015
	102	3		0.006	0.005	0.003	0.005

TABLE V-13 (Continued)

SECONDARY COPPER SAMPLING DATA
MISCELLANEOUS RAW WASTEWATER
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
122. lead	1	3		528	30	800	453
	102	3	<0.02	4			4
123. mercury	1	3		0.0091	0.1	0.0026	0.3723
	102	3	0.0001	0.0101			0.0101
124. nickel	1	3		0.56	4	2	2.19
	102	3	<0.005	0.3			0.3
125. selenium	1	3		0.018	0.55	0.3	0.289
	102	3	<0.01	<0.01			<0.01
128. zinc	1	3		1,374	40		707
	102	3	<0.06	40			40
Nonconventionals							
chemical oxygen demand (COD)	1	3		620	4,100		2,360
	102	1		82			82
fluoride							
total oxygen demand (TOC)	1	3		181	611		396
	102	1		22			22
phenols (total; by 4-AAP method)	1	3		2.6	1.34		1.97
	102	1		0.582	0.196	0.156	0.311

TABLE V-13 (Continued)

SECONDARY COPPER SAMPLING DATA
MISCELLANEOUS RAW WASTEWATER
RAW WASTEWATER

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Conventionals							
oil and grease	1	1		112	5		59
	102	1		11	7	28	15
total suspended solids (TSS)	1	3		9,220	80,500		44,860
	102	1		23			23
pH (standard units)	1	1		6.5	6.5	7	

(a),(b),(c) Reported together.

TABLE V-14

SECONDARY COPPER SAMPLING DATA
TREATMENT PLANT SAMPLES - PLANT A

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants(a)							
6. carbon tetrachloride	59	1		ND	0.264	ND	0.264
23. chloroform	59	1	0.011	0.045	0.234	0.024	0.101
66. bis(2-ethylhexyl) phthalate	59	3	0.1650	0.0140	*	0.1150	0.0430
68. di-n-butyl phthalate	59	3	*	*	*	*	*
69. di-n-octyl phthalate	59	3		ND	*	ND	*
78. anthracene (a)							
81. phenanthrene (a)	59	3		ND	<0.012	<0.011	<0.012
118. cadmium	59	3	<0.002	<0.002	<0.002	<0.002	<0.002
119. chromium	59	3	<0.005	<0.005	<0.005	<0.005	<0.005
120. copper	59	3	0.2	0.1	0.03	0.02	0.05
122. lead	59	3	<0.02	<0.02	<0.02	<0.02	<0.02
123. mercury	59	3	0.0001	0.0001	<0.0001	0.0001	<0.0001
124. nickel	59	3	<0.005	<0.005	0.02	<0.005	<0.010
126. silver	59	3	<0.02	<0.02	<0.02	<0.02	<0.02
128. zinc	59	3	<0.06	0.07	<0.06	<0.06	<0.02
Nonconventionals							
chemical oxygen demand (COD)	59	3	<5	11	35	13	20
phenols (total; by 4-AAP method)	59	2		0.005	0.005		0.005
total organic carbon (TOC)	59	3	5	4	53	5	21
Conventionals							
oil and grease	59	1		8	2	<1	<3
total suspended solids (TSS)	59	3	7	7	2	<1	<3
pH (standard units)	59	1		8.5	8.4	8.8	

(a) Reported together.

TABLE V-15

SECONDARY COPPER SAMPLING DATA
TREATMENT PLANT SAMPLES - PLANT B

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
23. chloroform	103	1	*	0.03	0.038	0.037	0.035
30. 1,2-trans-dichloroethylene	103	1	0.013	ND	0.014	*	0.007
66. bis(2-ethylhexyl) phthalate	103	3	0.144	0.506			0.506
68. di-n-butyl phthalate	103	3	*	0.0615			0.0615
69. di-n-octyl phthalate	103	3	*	0.184			0.184
80. fluorene	103	3	ND	0.07			0.07
118. cadmium	103	3	0.03	0.01			0.01
120. copper	103	3	<0.006	0.1			0.1
123. mercury	103	3	0.0001	0.0011			0.0011
128. zinc	103	3	<0.0600	<0.07			<0.07
Nonconventionals							
chemical oxygen demand (COD)	103	1		37			37
phenols (total; by 4-AAP method)	103	1		0.454	0.448	0.422	0.441
total organic carbon (TOC)	103	1		14			14
Conventionals							
oil and grease	103	1		5	8	14	9
total suspended solids (TSS)	103	1		<1			<1

TABLE V-16

SECONDARY COPPER SAMPLING DATA
TREATMENT PLANT SAMPLES - PLANT C

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
9. hexachlorobenzene	120	2	ND	0.219	0.169	ND	0.194
15. 1,1,2,2-tetrachloroethane	120	2	*	0.024	*	*	0.008
23. chloroform	120	2	0.043	0.018	*	*	0.006
39. fluoranthene	120	2	ND	*	*	0.017	0.006
66. bis(2-ethylhexyl) phthalate	120	2	*	0.06	ND	0.084	0.072
67. butyl benzyl phthalate	120	2	*	ND	ND	0.023	0.023
68. di-n-butyl phthalate	120	2	*	0.067	0.052	0.113	0.077
69. di-n-octyl phthalate	120	2	*	ND	*	0.015	0.008
70. diethyl phthalate	120	2	ND	0.082	ND	0.079	0.081
71. dimethyl phthalate	120	2	ND	1.271	0.8	0.551	0.874
74. 3,4-benzofluoranthene (a)	120	2	ND	ND	0.012	ND	0.012
75. benzo(k)fluoranthene (a)							
76. chrysene	120	2	*	ND	0.011	ND	0.011
78. anthracene (b)	120	2	ND	0.014	0.06	0.141	0.072
80. fluorene	120	2	ND	0.104	ND	0.074	0.089
81. phenanthrene (b)							
84. pyrene	120	2	*	0.027	0.016	0.038	0.027
85. tetrachloroethylene	120	2	*	0.024	*	*	0.008
115. arsenic	120	2	0.01	0.7	0.74	0.42	0.62
117. beryllium	120	2	0.001	0.4	0.2	0.5	0.4
118. cadmium	120	2	0.002	0.08	0.01	0.05	0.05
119. chromium	120	2	0.008	0.3	0.2	0.5	0.3
120. copper	120	2	0.008	70	30	90	63
121. cyanide	120	2		0.128	0.001	0.037	0.055
122. lead	120	2	0.02	50	20	60	43

TABLE V-16 (Continued)

SECONDARY COPPER SAMPLING DATA
TREATMENT PLANT SAMPLES - PLANT C

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
123. mercury	120	2	0.0001	0.0004	0.0002	0.001	0.0005
124. nickel	120	2	0.005	2	0.8	2	1.6
125. selenium	120	2	0.01	0.23	0.38	0.41	0.34
126. silver	120	2	0.02	0.05	0.06	0.09	0.07
127. zinc	120	2	0.06	200	100	300	200
Nonconventionals							
chemical oxygen demand (COD)	120	2		538	317	861	572
phenols (total; by 4-AAP method)	120	2		0.01	0.008	0.008	0.009
total organic carbon (TOC)	120	2		57	10	41	36
Conventionals							
oil and grease	120	2		21	8	32	20
total suspended solids (TSS)	120	2		2,918	1,582	5,250	3,251

(a),(b) Reported together.

TABLE V-17

SECONDARY COPPER SAMPLING DATA
TREATMENT PLANT SAMPLES - PLANT E

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Toxic Pollutants							
4. benzene	18	2		<0.118	ND	<0.03	<0.074
6. carbon tetrachloride	18	2		ND	ND	*	*
23. chloroform	18	2		0.116	0.48	0.101	0.232
30. 1,2-trans-di-chloro-ethylene	18	2		0.022	ND	0.011	0.017
44. methylene chloride	18	2		ND	0.59	ND	0.59
51. chlorodibromomethane	18	2		ND	ND	0.011	0.011
55. napthalene	13	3		ND	0.2	0.921	0.561
66. bis(2-ethylhexyl) phthalate	18	3		0.05	0.013	0.126	0.063
68. di-n-butyl phthalate	18	3		0.082	0.06	0.012	0.051
70. diethyl phthalate	18	3		ND	0.02	ND	0.02
71. dimethyl phthalate	18	3		ND	0.074	ND	0.074
80. fluorene	18	3		ND	0.046	ND	0.046
85. tetrachloroethylene	18	2		*	ND	*	*
86. toluene	18	2		ND	0.08	*	0.04
87. trichloroethylene	18	2		<0.311	ND	<0.081	<0.196
117. beryllium	18	3		0.03	0.04	<0.02	<0.02
118. cadmium	18	3		4	2	0.9	2.3
119. chromium	18	3		4	2	0.67	2.22
120. copper	18	3		30	30	20	27
121. cyanide	18	3		0.005	0.003	0.002	0.003
122. lead	18	3		70	4	3	26
123. mercury	18	3		0.0002	0.0002	0.0003	0.0002
124. nickel	18	3		510	300	140	317
128. zinc	18	3		160	100	40	100

TABLE V-17 (Continued)

SECONDARY COPPER SAMPLING DATA
TREATMENT PLANT SAMPLES - PLANT E

Pollutant	Stream Code	Sample Type	Source	Concentration (mg/l, except as noted) Day 1	Day 2	Day 3	Average
Nonconventionals							
chemical oxygen demand (COD)	18	2		1,970	1,250	596	1,272
fluoride	18	2		0.27	0.52	0.54	0.44
phenols (total; by 4-AAP method)	18	2		0.039	0.216	0.084	0.113
total organic carbon (TOC)	18	2		26	24	14	21
Conventionals							
oil and grease	18	1		7	2	4	4
total suspended solids (TSS)	18	2		175	205	210	197
pH (standard units)	18	1		2.58	3.75	4.6	

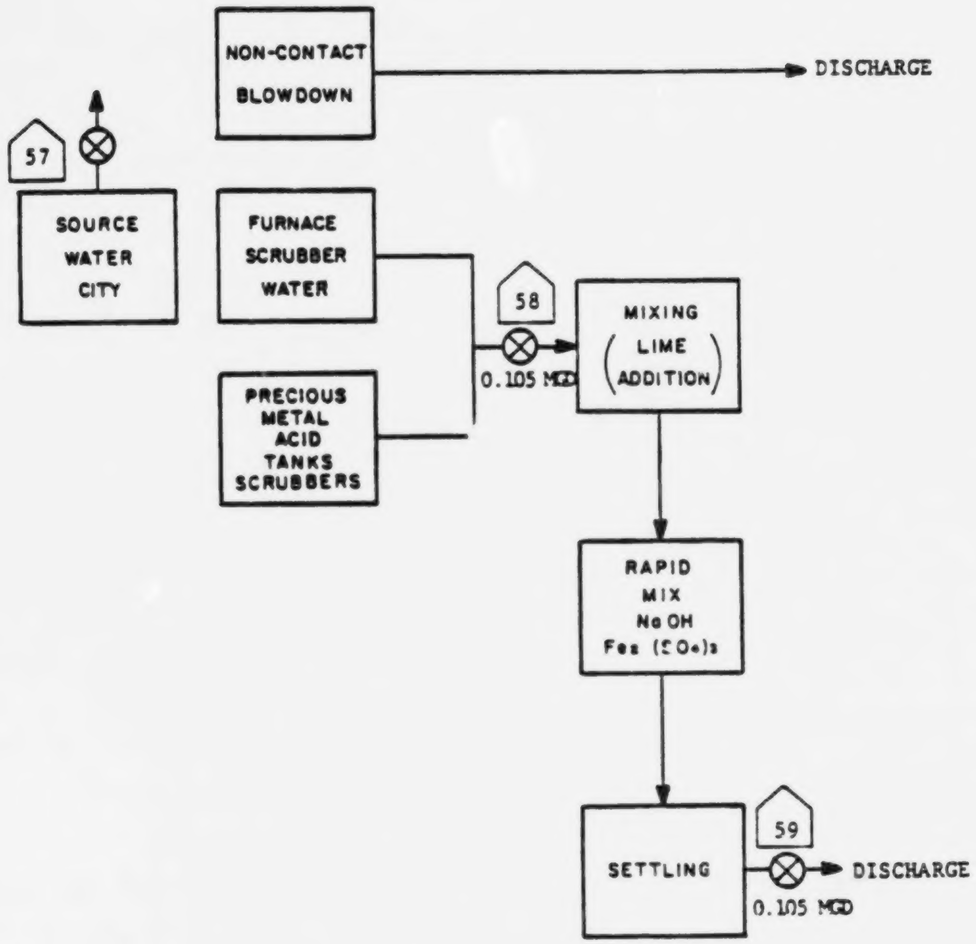
NON-CONTACT BLOWDOWN
DISCHARGE
57
SOURCE WATER CITY
FURNACE SCRUBBER WATER
PRECIOUS METAL ACID TANKS SCRUBBERS
58
0.105 MGD
MIXING (LIME ADDITION)
RAPID MIX NaOH $Fe_2(SO_4)_3$
SETTLING
59
DISCHARGE
0.105 MGD

FIGURE V-1

SAMPLING SITES AT SECONDARY COPPER PLANT A

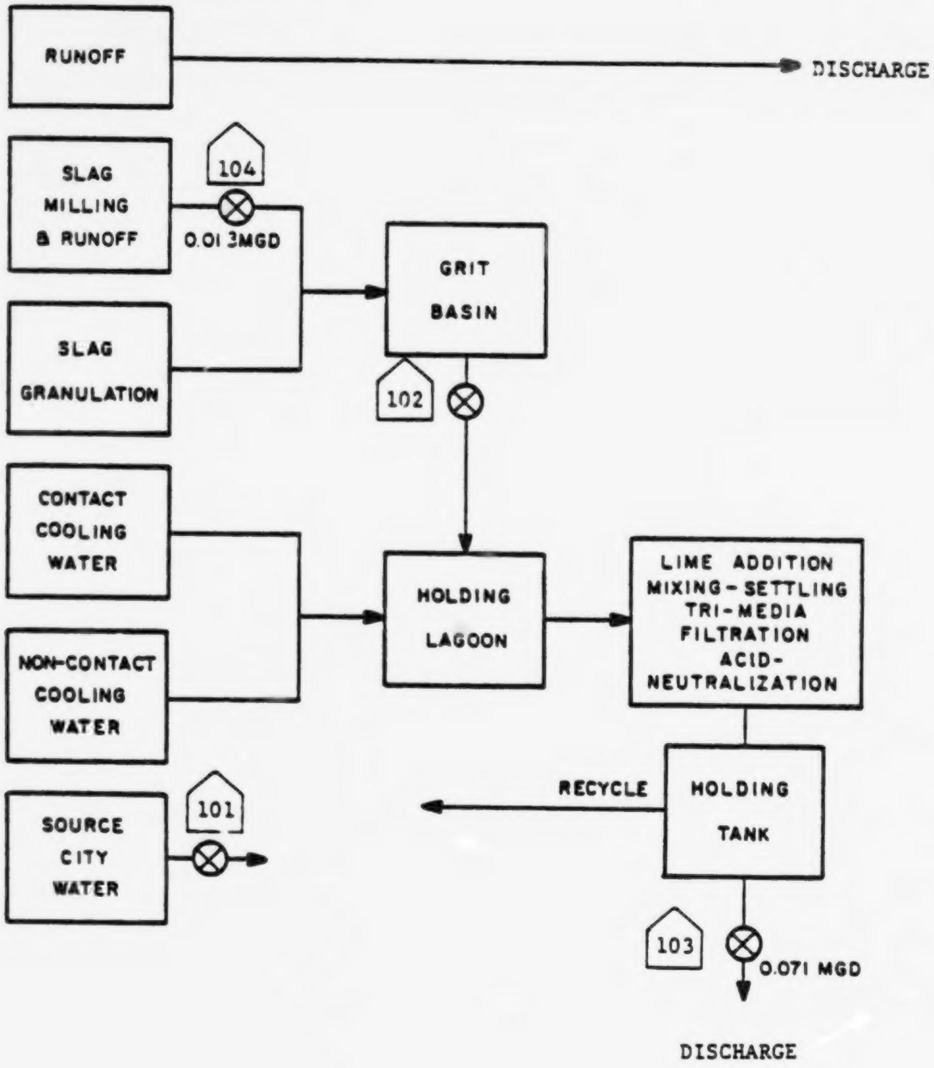
RUNOFF
DISCHARGE
SLAG MILLING & RUNOFF
104
0.013MGD
GRIT BASIN
SLAG GRANULATION
102
CONTACT COOLING WATER
NON-CONTACT COOLING WATER
HOLDING LAGOON
LIME ADDITION MIXING-SETTLING TRI-MEDIA FILTRATION ACID-NEUTRALIZATION
SOURCE CITY WATER
101
RECYCLE
HOLDING TANK
103
0.071 MGD
DISCHARGE

FIGURE V-2

SAMPLING SITES AT SECONDARY COPPER PLANT B

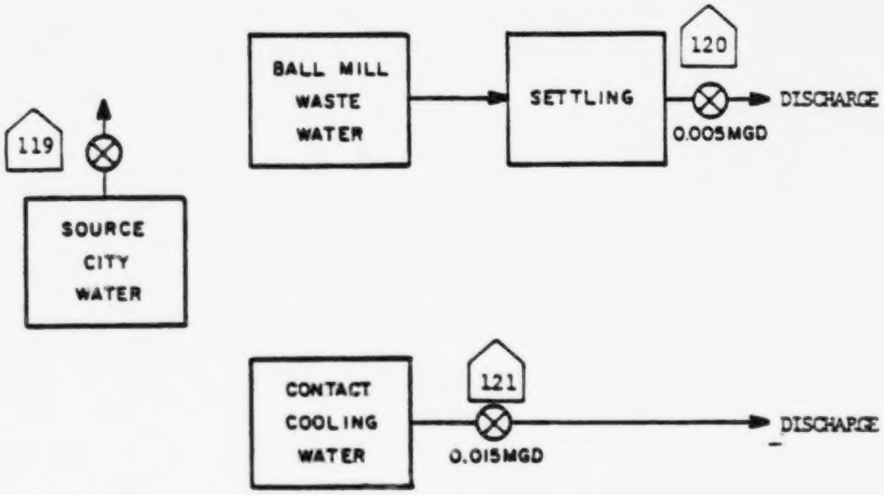
BALL MILL WASTE WATER
SETTLING
120
DISCHARGE
0.005MGD
119
SOURCE CITY WATER
CONTACT COOLING WATER
121
DISCHARGE
0.015MGD

FIGURE V-3

SAMPLING SITES AT SECONDARY COPPER PLANT C

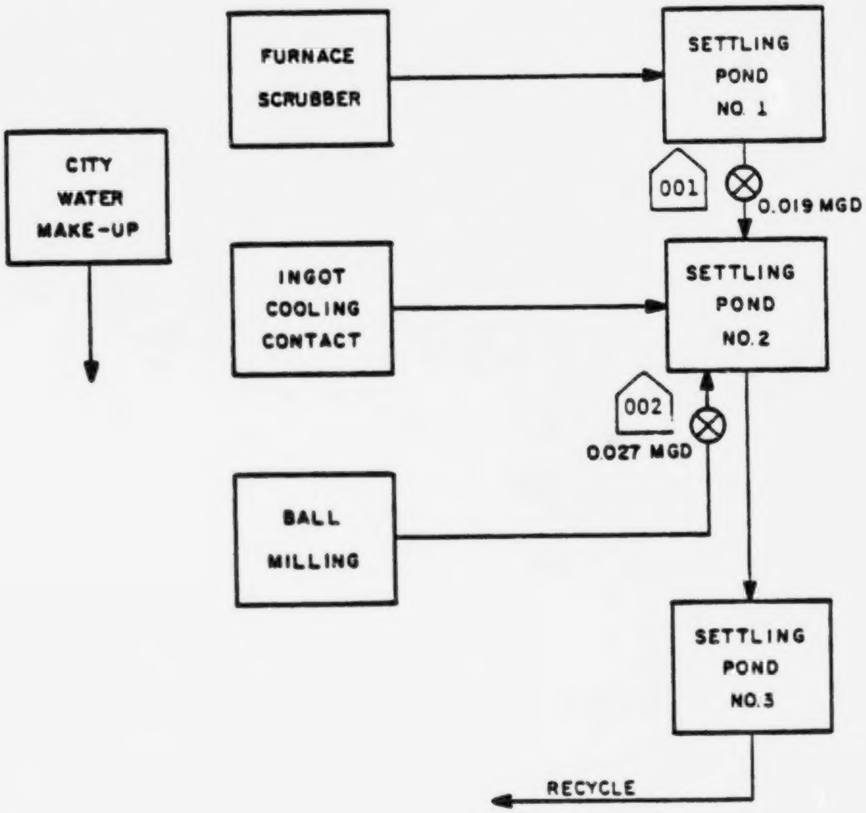
FURNACE SCRUBBER
SETTLING POND NO. 1
CITY WATER MAKE-UP
001
0.019 MGD
INGOT COOLING CONTACT
SETTLING POND NO. 2
002
0.027 MGD
BALL MILLING
SETTLING POND NO. 3
RECYCLE

FIGURE V-4

SAMPLING SITES AT SECONDARY COPPER PLANT D

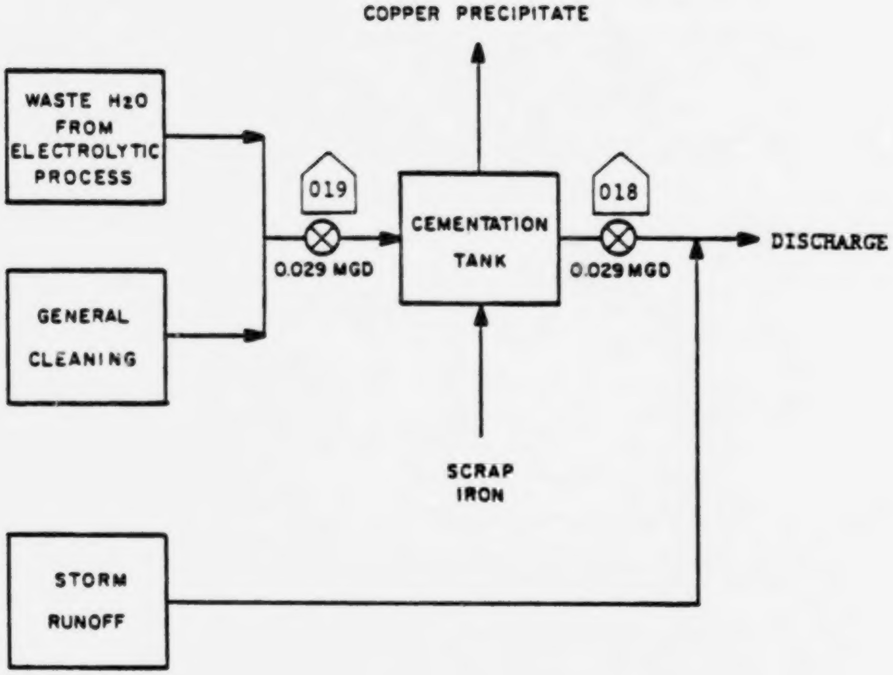
COPPER PRECIPITATE
WASTE H2O FROM ELECTROLYTIC PROCESS
GENERAL CLEANING
019
0.029 MGD
CEMENTATION TANK
018
0.029 MGD
DISCHARGE
SCRAP IRON
STORM RUNOFF

FIGURE V-5

SAMPLING SITES AT SECONDARY COPPER PLANT E

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

This section examines chemical analysis data presented in Section V from secondary copper plants and discusses the selection or exclusion of pollutants for potential limitation in this subcategory.

Each pollutant selected for potential limitation is discussed in Section VI of Vol. 1. That discussion provides information concerning where the pollutant originates (i.e., whether it is a naturally occurring substance, processed metal, or a manufactured compound); general physical properties and the form of the pollutant; toxic effects of the pollutant in humans and other animals; and behavior of the pollutant in POTW at the concentrations expected in industrial discharges.

The discussion that follows describes the analysis that was performed to select or exclude pollutants for further consideration for limitations and standards. Pollutants are selected for further consideration if they are present in concentrations treatable by the technologies considered in this analysis. The treatable concentrations used for the toxic metals were the long-term performance values achievable by lime precipitation, sedimentation, and filtration. The treatable concentrations for the toxic organics were the long-term performance values achievable by carbon absorption (see Section VII of Vol. 1 --Combined Metals Data Base).

After proposal, the Agency re-evaluated the treatment performance of activated carbon absorption to control toxic organic pollutants. The treatment performance for the acid extractable, base-neutral extractable, and volatile organic pollutants has been set equal to the analytical quantification limit of 0.010 mg/l. The analytical quantification limit for pesticides and total phenols (by 4-AAP method) is 0.005 mg/l, which is below the 0.010 mg/l accepted for the other toxic organics. However, to be consistent, the treatment performance of 0.010 mg/l is used for pesticides and total phenols. The 0.010 mg/l concentration is achievable, assuming enough carbon is used in the column and a suitable contact time is allowed.

The frequency of occurrence for 36 of the toxic pollutants has been redetermined based on the revised treatment performance value. However, no toxic organic pollutants have been selected for consideration for limitation.

CONVENTIONAL AND NONCONVENTIONAL POLLUTANT PARAMETERS

This study considered samples from the secondary copper subcategory for three conventional pollutant parameters (oil and

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grease, total suspended solids, and pH) and seven nonconventional pollutant parameters (aluminum, ammonia, chemical oxygen demand, chloride, fluoride, total organic carbon, and total phenols).

CONVENTIONAL POLLUTANT PARAMETERS SELECTED

The conventional pollutants and pollutant parameters selected for consideration for limitation in this subcategory are:

total suspended solids (TSS)
oil and grease
pH

Total suspended solids ranged from 3 to 8,790 mg/l. All samples had TSS concentrations above that considered achievable by identified treatment technology (2.6 mg/l). Furthermore, most of the technologies used to remove toxic metals do so by precipitating the metals. A limitation on total suspended solids ensures that sedimentation to remove precipitated toxic metals is effectively operating. Therefore, total suspended solids is selected for consideration for limitation.

Oil and grease concentrations in the wastewaters sampled ranged from 2 to 180 mg/l in 10 samples. Residue concentration is the principal source of these pollutants. The concentration in 2 of the 10 samples analyzed exceeded the treatable concentration (10 mg/l). Thus, this pollutant is selected for consideration for limitation.

The pH values observed ranged from 1.5 to 7.0. Effective removal of toxic metals by precipitation requires careful control of pH. Therefore, pH is considered for limitation in this subcategory.

TOXIC POLLUTANTS

The frequency of occurrence of the toxic pollutants in the wastewater samples taken is presented in Table VI-1 (page 1300). These data provide the basis for the categorization of specific pollutants, as discussed below. Table VI-1 is based on the raw wastewater data from streams 2, 104, 58, 19, and 121 (see Section V). Miscellaneous wastewater and treatment plant samples were not considered in the frequency count.

Toxic Pollutants Never Detected

The toxic pollutants listed in Table VI-2 (page 1304) were not detected in any wastewater samples from this subcategory. Therefore, they are not selected for consideration in establishing regulations.

Toxic Pollutants Never Found Above Their Analytical Quantification Level

The toxic pollutants listed below were never found above their analytical quantification concentration in any wastewater samples from this subcategory. Therefore, they are not selected for consideration in establishing regulations.

15. 1,1,2,2-tetrachloroethane
71. dimethyl phthalate
74. benzo(b)fluoranthene (a)
75. benzo(k)fluoranthene (a)
109. PCB-1232 (b)
110. PCB-1248 (b)
111. PCB-1260 (b)
112. PCB-1016 (b)
116. asbestos

(a), (b) Reported together as a combined value

Toxic Pollutants Present Below Concentrations Achievable by Treatment

The pollutants listed below are not selected for consideration in establishing limitations because they were not found in any wastewater samples from this subcategory above concentrations considered achievable by existing or available treatment technologies. These pollutants are discussed individually following the list.

114. antimony
117. beryllium
121. cyanide
123. mercury
126. silver

Antimony was detected above its analytical quantification limit in three of thirteen samples from five plants; however, these sample concentrations were below that attainable by treatment. Therefore, antimony is not selected for limitation.

Beryllium was detected above its analytical quantification limit in eight of thirteen samples from five plants; however, these sample concentrations were below that attainable by treatment. Therefore, beryllium is not selected for limitation.

Cyanide was detected above its analytical quantification limit in six of eleven samples from four plants; however, these sample concentrations were below that attainable by treatment. There fore, cyanide is not selected for limitation.

Mercury was detected at, or above, its 0.0001 mg/l analytical quantification limit in thirteen of thirteen samples from five plants. All of the values are below the 0.026 mg/l concentration considered achievable by identified treatment technology. Therefore, mercury is not considered for limitation.

Silver was detected above its analytical quantification limit in three of ten samples from four plants; however, these sample concentrations were below that attainable by treatment. Therefore, silver is not selected for limitation.

Toxic Pollutants Detected in a Small Number of Sources

Toxic pollutants detectable in the effluent from only a small number of sources within the subcategory and it is uniquely related to only those sources are not appropriate for limitation in a national regulation. The toxic pollutants listed in Table VI-3 (page 1306) were not selected for limitation on this basis.

Although these pollutants were not selected for consideration in establishing nationwide limitations, it may be appropriate, on a case-by-case basis, for the local permitter to specify effluent limitations.

Acenapthene was found above its analytical quantification limit in two of twelve samples from five plants. The detected concentrations were 0.019 mg/l and 0.036 mg/l in the spent electrolyte wastewater sample. Both of these values are above the concentration considered achievable by identified technology. However, since the third sampling date at the plant showed a "not detected" value, acenapthene is not considered for limitation because it is believed to be unique to that particular plant and is not expected to be a common pollutant in spent electrolyte wastewater.

Benzene was detected in three of twelve samples taken from four plants. Only one value was above its analytical quantification limit. The value was 0.019 mg/l which is above the 0.010 mg/l concentration considered attainable by identified technology. Because it was found at a treatable concentration in only one sample, benzene is not considered for limitation.

Carbon tetrachloride was found in just one of ten samples from four plants. The reported value was 0.116 mg/l, which is above the concentration considered achievable by identified technology. This pollutant was not detected in any of the other nine samples. Because it was found in just one sample, carbon tetrachloride is not considered for limitation.

1,2-Dichloroethane was detected in three of ten samples collected from four plants. The pollutant was found in two of four raw wastewater streams. Two of the detected values were above the 0.010 mg/l concentration considered achievable by identified treatment technology. Analyses of two other samples from the two raw wastewater streams that contained 1,2-dichloroethane did not detect this pollutant. Also, in the dcp, all of the secondary copper plants indicated that this pollutant was either known or believed to be absent. Therefore, 1,2-dichloroethane is not considered for limitation.

Chloroform, a common laboratory solvent, was detected above its analytical quantification limit in all ten samples from four plants. Also, it was found above the concentration considered achievable by identified technology in all ten samples, ranging from 1.11 mg/l to 1.19 mg/l. Concentrations above the analytical concentration limit in four blanks (0.070 mg/l, 0.181 mg/l, 0.127 mg/l, and 0.043 mg/l) analyzed raise the likelihood of sample contamination. Also, in the dcp, all of the secondary copper plants indicated that this pollutant was either known or believed to be absent. Chloroform, therefore, is not selected for consideration for limitation.

The toxic pollutants 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene are not clearly separated by the analytical protocol used in this study; thus, they are reported together. The sum of these pollutants was found above its analytical quantification limit in two of twelve samples from five plants. The detected concentrations were 0.117 mg/l and 0.113 mg/l in the spent electrolyte wastewater sample. Both of these values are above the concentration considered achievable by identified technology. However, since the third sampling day at the plant showed a "not detected" value, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene are not considered for limitation because they are believed to be unique to that particular plant and are not expected to be common pollutants in spent electrolyte wastewater.

1,1-Dichloroethylene was found in concentrations above its analytical quantification limit in two of ten samples from four plants. The values were 0.038 mg/l and 0.667 mg/l, which are above the 0.010 mg/l concentration considered achievable by identified treatment technology. Three other samples, that were from the same two raw wastewater streams in which 1,1-dichloroethylene concentration was detected, did not contain 1,1-dichloroethylene. Therefore, 1,1-dichloroethylene is not considered for limitation.

1,2-trans-dichloroethylene was found in concentrations above its analytical quantification limit in three of ten samples from four plants, with values ranging from 0.012 mg/l to 0.157 mg/l. All three concentrations are above the 0.010 mg/l concentration considered achievable by identified treatment technology. Two of seven samples reported as "not detected" were from the same two raw wastewater streams that did contain 1,2-trans-dichloroethylene. Therefore, 1,2-trans-dichloroethylene is not considered for limitation.

Fluoranthene was found above its analytical quantification limit in two of twelve samples from five plants. The detected concentrations were 0.069 mg/l and 0.258 mg/l in the spent electrolyte wastewater sample. One of these values is above the concentration considered achievable by identified technology. However, since the third sampling day at the plant showed a "not detected" value, fluoranthene is not considered for limitation because it is believed to be unique to that particular plant and is not expected to be a common pollutant in spent electrolyte wastewater.

Methylene chloride, a common laboratory solvent, was found above its analytical quantification limit in two of ten samples from four plants. The detected concentrations were 0.64 mg/l and 0.58 mg/l. Analyses of three other samples from the raw wastewater streams in which methylene chloride was found did not detect any methylene chloride. The presence of this pollutant is not attributable to materials or processes associated with the secondary copper subcategory. Therefore, methylene chloride is not considered for limitation.

Bis(2-ethylhexyl) phthalate was found above its analytical quantification limit in 11 of 12 samples from five plants. The concentrations observed ranged from 0.019 to 0.4 mg/l. The presence of this pollutant is not attributable to materials or processes associated with the secondary copper subcategory. It is commonly used as a plasticizer in laboratory and field sampling equipment. EPA suspects sample contamination as the source of this pollutant. Therefore, bis(2-ethylhexyl) phthalate is not considered for limitation.

Butyl benzyl phthalate was found above its analytical quantification limit in two of 12 samples from five plants. The concentrations were 0.011 and 0.056 mg/l. The presence of this pollutant is not attributable to materials or processes associated with the secondary copper subcategory. It is commonly used as a plasticizer in laboratory and field sampling equipment. EPA suspects sample contamination as the source of this pollutant. Therefore, butyl benzyl phthalate is not considered for limitation.

Di-n-butyl phthalate was found above its analytical quantification limit in seven of 12 samples from five plants. The concentrations observed ranged from 0.012 to 0.4 mg/l. All seven samples showed concentrations above the 0.010 mg/l treatable concentration. The presence of this pollutant is not attributable to materials or processes associated with the secondary copper subcategory. It is commonly used as a plasticizer in laboratory and field sampling equipment. EPA suspects sample contamination as the source of this pollutant. Therefore, di-n-butyl phthalate is not considered for limitation.

Di-n-octyl phthalate was found above its analytical quantification limit in one of 12 samples from five plants. The concentration observed was 0.067 mg/l. The presence of this pollutant is not attributable to materials or processes associated with the secondary copper subcategory. It is commonly used as a plasticizer in laboratory and field sampling equipment. EPA suspects sample contamination as the source of this pollutant. Therefore, di-n-octyl phthalate is not considered for limitation.

Diethyl phthalate was found above its analytical quantification limit in two of 12 samples from five plants. The concentrations observed were 0.042 mg/l and 0.083 mg/l. The presence of this pollutant is not attributable to materials or processes associated with the secondary copper subcategory. It is commonly used as a plasticizer in laboratory and field sampling equipment. EPA suspects sample contamination as the source of this pollutant. Therefore, diethyl phthalate is not considered for limitation.

Chrysene was detected above its analytical quantification limit in just one of 12 samples from five plants. Since it was found in only one sample, chrysene is not considered for limitation.

The toxic pollutants anthracene and phenanthrene are not clearly separated by the analytical protocol used in this study; thus, they are reported together as a combined value. The sum of these pollutants was measured at a concentration greater than the analytical quantification limit in one of 12 samples from five plants. The detected concentration was 0.1 mg/l, which is greater than the concentration considered attainable by identified technology. Because they were found at a treatable concentration in only one sample, anthracene and phenanthrene are not considered for limitation.

Pyrene was found above its analytical quantification limit in two of 12 samples from five plants. The detected concentrations were 0.159 mg/l and 0.204 mg/l in the spent electrolyte wastewater sample. Both of these values are above the concentration considered achievable by identified technology. However, since the third sampling day at the plant showed a "not detected" value, pyrene is not considered for limitation because it is believed to be unique to that particular plant and is not expected to be a common pollutant in spent electrolyte wastewater.

Tetrachloroethylene was found above its analytical quantification limit in one of 10 samples from four plants. The detected concentration was 0.072 mg/l, which is greater than the concentration considered attainable by identified technology.

Because it was found at a treatable concentration in only one sample, tetrachloroethylene is not considered for limitation.

Toluene was detected in two of ten samples collected and two of four raw wastewater streams from four plants. Both detected concentrations were above the 0.010 mg/l concentration considered achievable by identified treatment technology. Analyses of three other samples from the two raw wastewater streams containing toluene did not detect this pollutant. Also, in the dcp, all of the secondary copper plants indicated that this pollutant was either known or believed to be absent. Therefore, toluene is not considered for limitation.

Arsenic was found above its analytical quantification limit in seven of 13 samples taken from five plants. Concentrations ranged from 0.01 to 1 mg/l. Only one sample contained a concentration above the 0.34 mg/l considered attainable by identified technology. Because it was found at a treatable concentration in only one sample, arsenic is not considered for limitation.

Selenium was found above its analytical quantification limit in seven of 10 samples taken from four plants. Concentrations ranged from 0.005 to 0.5 mg/l. Only two samples contained a concentration above the 0.20 mg/l considered attainable by identified technology. Because it was found at a treatable concentration in only two samples, selenium is not considered for limitation.

Toxic Pollutants Selected for Further Consideration for Limitation

The toxic pollutants listed below are selected for further consideration in establishing limitations for this subcategory. The toxic pollutants selected are each discussed following the list.

55. naphthalene
77. acenaphthylene
87. trichlorethylene
118. cadmium
119. chromium
120. copper
122. lead
124. nickel
128. zinc

Naphthalene was found above its analytical quantification limit in three of 12 samples from five plants. The concentrations measured in the spent electrolyte were 0.042 mg/l, 5.0 mg/l, and 1.6 mg/l. All three of these values are above the 0.010 mg/l concentration attainable by identified treatment technology. Because it is present at treatable concentrations in this spent electrolyte stream, naphthalene is selected for further consideration for regulation.

Acenaphthylene was found above its analytical quantification limit in three of 12 samples from five plants. The concentrations measured in the spent electrolyte were 0.042 mg/l, 0.117 mg/l, and 0.113 mg/l. All of these values are above the 0.010 mg/l concentration available by identified treatment technology. Because it is present at treatable concentrations in this spent electrolyte stream, acenaphthylene is selected for further consideration for regulation.

Trichloroethylene was found above its analytical quantification limit in four of 10 samples from four plants. The concentrations measured in the residue concentration wastewater were 0.023 mg/l and 0.058 mg/l. Both of these values are above the 0.010 mg/l concentration attainable by identified treatment technology. Because it is present at treatable concentrations in this residue concentration stream, trichloroethylene is selected for further consideration for regulation.

Cadmium was measured above its analytical quantification limit in 10 of 13 samples, taken from five plants, with concentrations ranging from 0.006 to 2.0 mg/l. Seven samples were above the 0.049 mg/l concentration attainable by identified treatment technology. Therefore, cadmium is selected for further consideration for limitation.

Chromium was found above its analytical quantification limit in 11 of 13 samples, taken from five plants, with concentrations ranging from 0.008 to 5.0 mg/l. Eleven samples were above the 0.07 mg/l concentration attainable by identified treatment technology. Therefore, chromium is selected for further consideration for limitation.

Copper was measured above its analytical quantification limit in all 13 samples, taken from five plants, with concentrations ranging from 0.3 to 3,630 mg/l. Twelve samples were above the 0.39 mg/l concentration attainable by identified treatment technology. Therefore, copper is selected for further consideration for limitation.

Lead was found in concentrations above its analytical quantification limit in all 13 samples taken from five plants, with concentrations ranging from 0.2 to 40 mg/l. All 13 samples were above the 0.08 mg/l concentration attainable by identified treatment technology. Therefore, lead is selected for further consideration for limitation.

Nickel was measured above its analytical quantification limit in all 13 samples, taken from five plants, with concentrations ranging from 0.007 to 530 mg/l. Since nine samples were also above the 0.22 mg/l concentration attainable by identified treatment technology, nickel is selected for further consideration for limitation.

Zinc was measured above its analytical quantification concentration in all 12 samples taken from five plants, with concentrations ranging from 0.7 to 300 mg/l. All 12 samples were above the 0.23 mg/l concentration attainable by the identified treatment technology. Therefore, zinc is selected for further consideration for limitation.

TABLE VI-1

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
SECONDARY COPPER
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	ND	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
1. acenaphthene	0.010	0.010	5	12	10			
2. acrolein	0.010	0.010	4	10	10			2
3. acrylonitrile	0.010	0.010	4	10	10			
4. benzene	0.010	0.010	4	10	7	2		1
5. benzidine	0.010	0.010	5	12	12			
6. carbon tetrachloride	0.010	0.010	4	10	9			1
7. chlorobenzene	0.010	0.010	4	10	10			
8. 1,2,4-trichlorobenzene	0.010	0.010	5	12	12			
9. hexachlorobenzene	0.010	0.010	5	12	12			
10. 1,2-dichloroethane	0.010	0.010	4	10	7	1		2
11. 1,1,1-trichloroethane	0.010	0.010	4	10	10			
12. hexachloroethane	0.010	0.010	5	12	12			
13. 1,1-dichloroethane	0.010	0.010	4	10	10			
14. 1,1,2-trichloroethane	0.010	0.010	4	10	10			
15. 1,1,2,2-tetrachloroethane	0.010	0.010	4	10	8	2		
16. chloroethane	0.010	0.010	4	10	10			
17. bis(chloromethyl) ether	0.010	0.010	4	10	10			
18. bis(2-chloroethyl) ether	0.010	0.010	5	12	12			
19. 2-chloroethyl vinyl ether	0.010	0.010	4	10	10			
20. 2-chloronaphthalene	0.010	0.010	5	12	12			
21. 2,4,6-trichlorophenol	Not Analyzed							
22. parachlorometa cresol	Not Analyzed							
23. chloroform	0.010	0.010	4	10				10
24. 2-chlorophenol	Not Analyzed							
25. 1,2-dichlorobenzene (c)	0.010	0.010	5	12	10			2
26. 1,3-dichlorobenzene (c)	0.010	0.010	5	12	10			2
27. 1,4-dichlorobenzene (c)	0.010	0.010	5	12	10			2
28. 3,3'-dichlorobenzidine	0.010	0.010	5	12	12			
29. 1,1-dichloroethylene	0.010	0.010	4	10	8			2
30. 1,2-trans-dichloroethylene	0.010	0.010	4	10	7			3
31. 2,4-dichlorophenol	Not Analyzed							
32. 1,2-dichloropropane	0.010	0.010	4	10	10			
33. 1,3-dichloropropylene	0.010	0.010	4	10	10			
34. 2,4-dimethylphenol	Not Analyzed							
35. 2,4-dinitrotoluene	0.010	0.010	5	12	12			
36. 2,6-dinitrotoluene	0.010	0.010	5	12	12			
37. 1,2-diphenylhydrazine	0.010	0.010	5	12	12			

TABLE VI-1 (Continued)

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
SECONDARY COPPER
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	ND	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
38. ethylbenzene	0.010	0.010	4	10	10			
39. fluoranthene	0.010	0.010	5	12	7	3		2
40. 4-chlorophenyl phenylether	0.010	0.010	5	12	12			
41. 4-bromophenyl phenyl ether	0.010	0.010	5	12	12			
42. bis(2-chloroisopropyl)ether	0.010	0.010	5	12	12			
43. bis(2-chloroethoxy) methane	0.010	0.010	5	12	12			
44. methylene chloride	0.010	0.010	4	10	8			2
45. methyl chloride	0.010	0.010	4	10	10			
46. methyl bromide	0.010	0.010	4	10	10			
47. bromoform	0.010	0.010	4	10	10			
48. dichlorobromomethane	0.010	0.010	4	10	10			
49. trichlorofluoromethane	0.010	0.010	4	10	10			
50. dichlorodifluoromethane	0.010	0.010	4	10	10			
51. chlorodibromomethane	0.010	0.010	4	10	10			
52. hexachlorobutadiene	0.010	0.010	5	12	12			
53. hexachlorocyclopentadiene	0.010	0.010	5	12	12			
54. isophorone	0.010	0.010	5	12	12			
55. naphthalene	0.010	0.010	5	12	9			3
56. nitrobenzene	0.010	0.010	5	12	12			
57. 2-nitrophenol	Not Analyzed							
58. 4-nitrophenol	Not Analyzed							
59. 2,4-dinitrophenol	Not Analyzed							
60. 4,6-dinitro-o-cresol	Not Analyzed							
61. N-nitrosodimethylamine	0.010	0.010	5	12	12			
62. N-nitrosodiphenylamine	0.010	0.010	5	12	12			
63. N-nitrosodi-n-propylamine	0.010	0.010	5	12	12			
64. pentachlorophenol	Not Analyzed							
65. phenol	Not Analyzed							
66. bis(2-ethylhexyl) phthalate	0.010	0.010	5	12	10		1	1
67. butyl benzyl phthalate	0.010	0.010	5	12	8	2		2
68. di-n-butyl phthalate	0.010	0.010	5	12	2	3		7
69. di-n-octyl phthalate	0.010	0.010	5	12	8	3		1
70. diethyl phthalate	0.010	0.010	5	12	8	2		2
71. dimethyl phthalate	0.010	0.010	5	12	9	3		
72. benzo(a)anthracene	0.010	0.010	5	12	12			
73. benzo(a)pyrene	0.010	0.010	5	12	12			
74. 3,4-benzofluoranthene (d)	0.010	0.010	5	12	11	1		

TABLE VI-1 (Continued)

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
SECONDARY COPPER
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	ND	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
75. benzo(k)fluoranthene (d)	0.010	0.010	5	12	11	1		
76. chrysene	0.010	0.010	5	12	10	1		1
77. acenaphthylene	0.010	0.010	5	12	9			3
78. anthracene (e)	0.010	0.010	5	12	7	4		1
79. benzo(ghi)perylene	0.010	0.010	5	12	12			
80. fluorene	0.010	0.010	5	12	12			
81. phenanthrene (e)	0.010	0.010	5	12	7	3		1
82. dibenzo(a,h)anthracene	0.010	0.010	5	12	12			
83. indeno(1,2,3-cd)pyrene	0.010	0.010	5	12	12			
84. pyrene	0.010	0.010	5	12	7	3		2
85. tetrachloroethylene	0.010	0.010	4	10	5	4		1
86. toluene	0.010	0.010	4	10	8			2
87. trichloroethylene	0.010	0.010	4	10	5	1		4
88. vinyl chloride	0.010	0.010	4	10	10			
89. aldrin	0.005	0.010	5	10	10			
90. dieldrin	0.005	0.010	5	10	10			
91. chlordane	0.005	0.010	5	10	10			
92. 4,4'-DDT	0.005	0.010	5	10	10			
93. 4,4'-DDE	0.005	0.010	5	10	10			
94. 4,4'-DDD	0.005	0.010	5	10	10			
95. alpha-endosulfan	0.005	0.010	5	10	10			
96. beta-endosulfan	0.005	0.010	5	10	10			
97. endosulfan sulfate	0.005	0.010	5	10	10			
98. endrin	0.005	0.010	5	10	10			
99. endrin aldehyde	0.005	0.010	5	10	10			
100. heptachlor	0.005	0.010	5	10	10			
101. heptachlor epoxide	0.005	0.010	5	10	10			
102. alpha-BHC	0.005	0.010	5	10	10			
103. beta-BHC	0.005	0.010	5	10	10			
104. gamma-BHC	0.005	0.010	5	10	10			
105. delta-BHC	0.005	0.010	5	10	10			
106. PCB-1242 (f)	0.005	0.010	5	10	10			
107. PCB-1254 (f)	0.005		5	10	10			
108. PCB-1221 (f)	0.005		5	10	10			
109. PCB-1232 (g)	0.005	0.010	5	10	8	2		
110. PCB-1248 (g)	0.005		5	10	8	2		
111. PCB-1260 (g)	0.005		5	10	8	2		
112. PCB-1016 (g)	0.005		5	10	8	2		

Table VI-1 (Continued)

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
SECONDARY COPPER
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	ND	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
113. toxaphene	0.005	0.010	5	10	10			
114. antimony	0.100	0.47	5	13	10		3	
115. arsenic	0.010	0.34	5	13	6		6	1
116. asbestos	10 MF	10 MFL	1	1		1		
117. beryllium	0.010	0.20	5	13	3		8	
118. cadmium	0.002	0.049	5	13	3		3	7
119. chromium	0.005	0.07	5	13	2			11
120. copper	0.009	0.39	5	13			1	12
121. cyanide	0.02(f)	0.047	4	11	5		6	
122. lead	0.020	0.08	5	13				13
123. mercury	0.0001	0.036	5	13			13	
124. nickel	0.005	0.22	5	13			4	9
125. selenium	0.01	0.20	4	10	3		5	2
126. silver	0.02	0.07	4	10	7		3	
127. thallium	0.100	0.34	4	10	10			
128. zinc	0.050	0.23	5	12				12
129. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	Not analyzed							

(a) Analytical quantification concentration was reported with the data (see Section V).

(b) Treatable concentrations are based on performance of lime precipitation, sedimentation, and filtration for toxic metal pollutants and activated carbon adsorption for toxic organic pollutants.

(c),(d),(e),(f),(g) Reported together.

(h) Analytical quantification concentration for EPA Method 335.2, Total Cyanide Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March, 1979.

TABLE VI-2

TOXIC POLLUTANTS NEVER DETECTED

2. acrolein
3. acrylonitrile
5. benzidine
7. chlorobenzene
8. 1,2,4-trichlorobenzene
9. hexachlorobenzene
11. 1,1,1-trichloroethane
12. hexachloroethane
13. 1,1-dichloroethane
14. 1,1,2-trichloroethane
16. chloroethane
17. DELETED
18. bis(2-chloroethyl) ether
19. 2-chloroethyl vinyl ether
20. 2-chloronaphthalene
21. 2,4,6-trichlorophenol
22. parachlorometa cresol
24. 2-chlorophenol
28. 3,3'-dichlorobenzidiene
31. 2,4-dichlorophenol
32. 1,2-dichloropropane
33. 1,3-dichloropropylene
34. 2,4-dimethylphenol
35. 2,4-dinitrotoluene
36. 2,6-dinitrotoluene
37. 1,2-diphenylhydrazine
38. ethylbenzene
40. 4-chlorophenyl phenyl ether
41. 4-bromophenyl phenyl ether
42. bis(2-chloroisopropyl) ether
43. bis(2-chloroethoxy) methane
45. methyl chloride
46. methyl bromide
47. bromoform
48. dichlorobromomethane
49. DELETED
50. DELETED
51. chlorodibromomethane
52. hexachlorobutadiene
53. hexachlorocyclopentadiene
54. isophorone
56. nitrobenzene
57. 2-nitrophenol
58. 4-nitrophenol
59. 2,4-dinitrophenol
60. 4,6-dinitro-o-cresol
61. N-nitrosodimethylamine
62. N-nitrosodiphenylamine
63. N-nitrosodi-n-propylamine
64. pentachlorophenol
65. phenol

TABLE VI-2 (Continued)

TOXIC POLLUTANTS NEVER DETECTED

72. benzo(a)anthracene
73. benzo(a)pyrene
79. benzo(ghi)perylene
80. fluorene
82. dibenzo(a,h)anthracene
83. ideno(1,2,3-cd)pyrene
88. vinyl chloride
89. aldrin
90. dieldrin
91. chlordane
92. 4-4'-DDT
93. 4-4'-DDE
94. 4-4'-DDD
95. alpha-endosulfan
96. beta-endosulfan
97. endosulfan sulfate
98. endrin
99. endrin aldehyde
100. heptachlor
101. heptachlor epoxide
102. alpha-BHC
103. beta-BHC
104. gamma-BHC
105. delta-BHC
106. PCB-1242 (a)
107. PCB-1254 (a)
108. PCB-1221 (a)
113. toxaphene
127. thallium
129. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

(a) Reported together as a single value

TABLE VI-3

TOXIC POLLUTANTS DETECTED IN A SMALL NUMBER OF SOURCES

1. acenapthene
4. benzene
6. carbon tetrachloride
10. 1,2-dichloroethane
23. chloroform
25. 1,2-dichlorobenzene (a)
26. 1,3-dichlorobenzene (a)
27. 1,4-dichlorobenzene (a)
29. 1,1-dichloroethylene
30. 1,2-*trans*-dichloroethylene
39. fluoranthene
44. methylene chloride
66. bis(2-ethylhexyl) phthalate
67. butyl benzyl phthalate
68. di-n-butyl phthalate
69. di-n-octyl phthalate
70. diethyl phthalate
76. chrysene
78. anthracene (b)
81. phenanthrene (b)
84. pyrene
85. tetrachloroethylene
86. toluene
115. arsenic
125. selenium

(a), (b) Reported together as a combined value

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

The preceding sections of this supplement discussed the wastewater sources, flows, and characteristics of the wastewaters from secondary copper plants. This section summarizes the description of these wastewaters and indicates the treatment technologies which are currently practiced by the secondary copper subcategory for each waste stream.

TECHNICAL BASIS OF PROMULGATED BPT

EPA promulgated BPT effluent limitations for the secondary copper subcategory on February 27, 1975 under Subpart F of 40 CFR Part 421. These effluent limitations prohibit the discharge of process wastewater pollutants into navigable waters, and are based on control technologies for specific waste streams. The best practicable control technology for process wastewater generated during the contact cooling of copper ingots, anodes, billets, or shot is the elimination of this discharge through recycle and reuse of all contact cooling water. With the reuse and recycle of casting contact cooling water, the needs for solids and oil removal would be dictated by plant operational procedures. Removal of solids such as charcoal used to cover copper alloy ingots and the oxide scale and mold wash from anode casting requires sedimentation and filtration before the water is reused. The pond used for sedimentation will also provide cooling. Alternately, a cooling tower can provide settling and cooling capacity.

The best practicable control technology for process wastewater generated from the quenching and granulation of copper-rich slags is the elimination of this discharge by the recycle and reuse of all slag granulation wastewater. Suspended solids are removed by sedimentation and filtration prior to recycle and reuse. Alternately, the molten slag may be air cooled after it has been cast into slag pots for subsequent metal recovery by dry methods. When quenching and granulating depleted (waste) slags, the best practicable control technology is the total recycle and reuse of this wastewater after treatment to reduce suspended solids by sedimentation and filtration.

The best practicable control technology for process wastewater generated during copper-rich slag milling and classifying (residue concentration) is the elimination of this discharge by either total recycle and reuse of this wastewater, or by melt agglomerating the metal in a blast, cupola, or rotary furnace.

Prior to recycle and reuse, solids are removed by lime precipitation, if necessary, sedimentation, and filtration.

The best practicable control technology for process wastewater produced from furnace exhaust scrubbing is the elimination of wastewater discharge by recycling all of the furnace scrubber water. Before recycling, the scrubber water is treated by sedimentation and filtration or centrifugation. Another alternative to the elimination of this waste stream is conversion to dry air pollution control equipment.

The best practicable control technology for wastewater from electrolytic refining is the elimination of this wastewater discharge by treating the bleed stream from electrolytic cell operations, so that it is suitable for reuse in other plant processes. The treatment consists of removal of copper by cementation with iron metal, lime precipitation, and sand filtering this stream to remove solids. The resulting water is then discharged to a combined process wastewater reservoir serving other plant water needs.

CURRENT CONTROL AND TREATMENT PRACTICES

This section presents a summary of the control and treatment technologies that are currently applied to each of the sources generating wastewater in this subcategory. As discussed in Section V, wastewater associated with the secondary copper subcategory is characterized by the presence of the toxic metal pollutants and suspended solids. This analysis is supported by raw (untreated) wastewater data presented for specific sources as well as combined waste streams in Section V. Generally, these pollutants are present in each of the waste streams at treatable concentrations, so these waste streams are commonly combined for treatment to reduce the concentrations of these pollutants. Construction of one wastewater treatment system for combined treatment allows plants to take advantage of economies of scale and, in some instances, to combine streams of differing alkalinity to reduce treatment chemical requirements.

Six plants in this subcategory treat combined wastewater. At three of these plants, combined waste streams are settled in one or more settling ponds and then completely recycled. One plant treats combined wastewater by screening, sedimentation in ponds, and filtration, and combined wastewater is neutralized with caustic prior to discharge at another plant. At the remaining plant, combined waste streams are treated by lime precipitation, sedimentation, and filtration prior to discharge.

Residue Concentration

Residue concentration wastewater is generated when the copper value is recovered from reverberatory and rotary furnace slags, and other residues such as drosses, skimmings, spills, and sweepings, through wet milling and classifying. Seven plants generate this waste stream. Five of these plants achieve zero discharge of residue concentration wastewater through 100 percent recycle. One discharging plant does not recycle this waste stream and the other discharging plant did not report its recycle practices.

The residue concentration wastewater is treated by six of the seven plants prior to recycle or discharge. The treatment schemes include the following:

1. Preliminary treatment consisting of acid neutralization, polymer flocculation, and sedimentation for residue concentration wastewater only. Following preliminary treatment, the residue concentration wastewater is combined with other process wastewater and settled in lagoons, screened, filtered, and then completely recycled.

2. Sedimentation with lagoons, total recycle (combined treatment).

3. Filtration, total recycle (no combined treatment).

4. Sedimentation with classifiers and jigs, screening, sedimentation with lagoons, total recycle (no combined treatment).

5. Sedimentation in lagoons, discharge (no recycle, or combined treatment).

6. Grit removal for residue concentration wastewater, and combined treatment consisting of lime precipitation, sedimentation, and filtration, followed by discharge (recycle practices not reported).

The seventh plant recycles 100 percent of this waste stream, but did not report if the stream is treated prior to recycle.

Residue concentration wastewater is characterized by treatable concentrations of suspended solids and dissolved toxic metal pollutants.

Slag Granulation

This wastewater is generated when blast or cupola furnace slag is granulated with high pressure water jets, or in quench pits. Five plants generate a slag granulation waste stream. Four of these plants practice complete recycle, and the remaining plant evaporates its slag granulation wastewater. Prior to recycle, the slag granulation wastewater is treated by one or more of the following steps:

1. Screening,
2. Settling ponds or basins, and
3. Filtration.

At two of the total recycle plants, the slag granulation water is combined with other process wastewater when treated.

Slag granulation wastewater contains treatable concentrations of dissolved metals and suspended solids.

Reverberatory and Rotary Furnace Wet Air Pollution Control

Wet air pollution control devices are used by five secondary copper plants to contain metal oxide fumes and dust produced from rotary and reverberatory furnace operations. Three of the five plants completely recycle this waste stream, and one plant recycles 81 percent. The remaining plant does not recycle this waste stream. The control and treatment practices of the five plants are as follows:

1. Settling ponds, total recycle;
2. Settling ponds (combined with other process wastewater), total recycle;
3. Settling tanks, centrifuge, total recycle;
4. Holding tank, 81 percent recycle, settling tanks, discharge; and
5. Lime and caustic neutralization, flocculation with iron salts and polymers, clarification, and filtration followed by discharge.

As shown above, only one of the five plants combines it furnace wet air pollution control water with other process wastewater for treatment.

Reverberatory and rotary furnace wet air pollution control water is characterized by treatable concentrations of suspended solids and dissolved toxic metals.

Scrap Anode Rinsing

This wastewater is generated when anodes are removed from electrolytic cells and rinsed before further processing. Two plants rinse scrap anodes. Both plants recycle or reuse 100 percent of their scrap anode rinse water. This wastewater is characterized by treatable concentrations of suspended solids and dissolved toxic metal pollutants.

Spent Electrolyte

Electrolyte is continuously circulated through thickeners and filters to remove anode mud slimes, and recycled back through the electrolytic cells. A bleed stream is necessary to prevent the build-up of nickel and copper in the electrolyte. Usually, nickel or copper is recovered from the electrolyte bleed before recycle or discharge. Copper is recovered from the electrolyte by cementation with iron. In this process, scrap iron is added to the spent electrolyte and the solution is heated to about

$180^{\circ}F$, where copper precipitates from solution. An alternate method for recovering copper from solution is electrowinning. Nickel is recovered by evaporating the electrolyte bleed to produce nickel sulfate crystals and sulfuric acid. Six plants in the secondary copper subcategory have an electrolytic refining process. Two of those plants discharge spent electrolyte without treatment. One of those two plants contract hauls the spent electrolyte. At two plants, copper is cemented from an electrolytic bleed stream with iron, and the resulting solution is either discharged (at one plant) or contract hauled (at the other plant). The remaining two plants each achieve zero discharge of spent electrolyte through the following treatment schemes:

1. An electrolyte bleed stream is electrowinned to recover copper and evaporated to recover nickel sulfate crystals and sulfuric acid.

2. An electrolyte bleed stream is evaporated to recover nickel sulfate and sulfuric acid.

Spent electrolyte is acidic and contains treatable concentrations of dissolved metals (particularly copper).

Casting Contact Cooling

Contact cooling water is used by 22 plants in the secondary copper subcategory. As discussed in Section III, there are a variety of methods for cooling the various types of castings. In the case of ingots, anodes, and billets, the molten metal is solidified by spray cooling, and then quenched in tanks. Finished refined copper shapes are usually prepared by cooling the molten metal by non-contact cooling techniques, and then quenching the solidified metal. Shot is manufactured by directing a small stream of molten copper directly into a quench pit.

Eleven of the 22 plants which produce casting contact cooling water achieve zero discharge through total recycle. One achieves zero discharge through dry well injection. There are a variety of control and treatment practices utilized by both zero discharge and discharging plants. These control and treatment practices are as follows:

1. No recycle, discharge without treatment (five plants);

2. Partial recycle, caustic neutralization, discharge (one plant);

3. Cooling pond, partial recycle, settling pond, discharge (one plant);

4. Partial recycle through cooling towers (two plants);

5. 99 percent recycle with a blowdown stream treated by

lime precipitation, sedimentation, and filtration prior to discharge (one plant);

6. No treatment, total recycle (three plants);
7. Screening, total recycle (one plant);
8. Settling, total recycle (four plants);
9. Screening, settling, filtration, total recycle (one plant);
10. Settling pits, holding tanks, cooling tower, centrifuge, total recycle (one plant);
11. Neutralization with lime, flocculation with polymers, settling, total recycle (one plant); and
12. No recycle, dry well injection (one plant).

At five of the above plants, casting contact cooling water is combined with other process wastewater when treated.

Casting contact cooling water is characterized by treatable concentrations of lead, zinc, copper, and total suspended solids.

Casting Wet Air Pollution Control

Three plants control fumes from casting operations with wet air pollution control devices. One plant completely recycles casting scrubber water after neutralization with caustic and settling, and one plant contract hauls a casting scrubber water bleed stream. The remaining plant discharges a casting scrubber water bleed stream after neutralization with caustic.

CONTROL AND TREATMENT OPTIONS CONSIDERED

Based on an examination of the wastewater sampling data, three control and treatment options that effectively control the pollutants found in secondary copper wastewaters were selected for evaluation. These technology options are discussed below.

Reverse osmosis (Option F) is theoretically applicable to waste waters generated in the secondary copper subcategory; however, it is not demonstrated in the nonferrous metals manufacturing category, nor is it clearly transferable. Activated alumina absorption (Option D) and activated carbon absorption (Option E) were not considered for secondary copper because pollutants (arsenic, fluoride and the toxic organics) generally treatable by these technologies are not present at treatable concentrations or in quantities warranting control.

OPTION A

Option A for the secondary copper subcategory is equivalent to the technology basis for the promulgated pretreatment standards for existing sources. The Option A treatment scheme consists of chemical precipitation and sedimentation (lime and settle) applied to combined waste streams. Chemical precipitation and sedimentation consists of lime addition to precipitate metals followed by gravity sedimentation for the removal of suspended solids, including the metal precipitates.

OPTION G

Option G for the secondary copper subcategory is based on total recycle of all process wastewater with lime precipitation and sedimentation treatment. In-process flow reduction prior to lime and settle treatment is also included for casting contact cooling and furnace scrubber liquor. Flow reduction for these two waste streams is based on cooling towers and holding tanks, respectively. The water obtained from lime and settle treatment is of sufficient quality for reuse in secondary copper operations.

SECTION VIII

COSTS, ENERGY, AND NONWATER QUALITY ASPECTS

This section describes the method used to develop the costs associated with the control and treatment technologies of Options A and G discussed in Section VII for wastewaters from secondary copper plants. Plant-by-plant compliance costs for these options were revised following the 1983 proposal. These revisions calculate incremental costs, above treatment already in place, necessary to comply with these effluent limitations and standards. The energy requirements of the considered options as well as solid waste and air pollution aspects are also discussed.

TREATMENT OPTIONS COSTED FOR EXISTING SOURCES

As discussed in Section VII, two treatment options have been developed for secondary copper sources. The options are summarized below and schematically presented in Figures XII-1 and XII-2 (pages 1333 and 1334).

OPTION A

Option A consists of lime precipitation and sedimentation end-of-pipe technology.

OPTION G

Option G consists of in-process flow reduction measures and lime precipitation and sedimentation end-of-pipe technology. The in-process flow reduction measure consists of the recycle of scrubber water through holding tanks and recycle of casting contact cooling water through cooling towers.

Cost Methodology

Plant-by-plant compliance costs have been estimated for the secondary copper subcategory and are presented in the administrative record supporting this regulation. A comparison of the costs developed for proposal and the revised costs for the final regulation are presented in Table VIII-1 (page 1318) for the indirect dischargers. EPA is promulgating BAT effluent limitations equivalent to those established in 1975 with the exception of storm water. With this rulemaking, EPA has eliminated the net monthly precipitation allowance. These guidelines are based on cooling impoundments rather than settling and evaporative impoundments. Cooling impoundments require much smaller surface areas than the settling and evaporative impoundments for which the net precipitation discharge was allowed. Costs for cooling towers were developed for BAT in the 1975 rulemaking for when a plant had insufficient existing impoundment capacity or cooling impoundments were not feasible due to space limitations. EPA believes that secondary copper

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plants can accommodate the small volume of water resulting from net precipitation on cooling impoundments. There is no cost associated with the modified BAT effluent limitations.

Each of the major assumptions used to develop compliance costs is presented in Section VIII of Vol. 1. However, each subcategory contains a unique set of waste streams requiring certain subcategory-specific assumptions to develop compliance costs. Three major assumptions are discussed briefly below.

(1) Monitoring costs are not included for 100 percent recycle since the option is zero discharge.

(2) Where equipment of sufficient treatment capacity is in place, annual costs are not included since these were incurred by the existing PSES regulation. However, costs for cooling towers, which were not included under promulgated PSES are included for this regulation.

(3) No cost is included for direct dischargers to comply with elimination of net precipitation allowances.

NONWATER QUALITY ASPECTS

A general discussion of the nonwater quality aspects of the control and treatment options considered for the nonferrous metals category is contained in Section VIII of Vol. 1. Nonwater quality impacts specific to the secondary copper subcategory, including energy requirements, solid waste and air pollution are discussed below.

ENERGY REQUIREMENTS

The methodology used for determining the energy requirements for the various options is discussed in Section VIII of the General Development Document. Energy requirements for the two options considered are estimated at 0.15 MW hr/yr and 0.18 MW hr/yr for Options A and G, respectively. Option G represents roughly one percent of a typical plant's electrical usage. It is therefore concluded that the energy requirements of the treatment options considered will have no significant impact on total plant energy consumption.

SOLID WASTE

Sludge generated in the secondary copper subcategory is due to the precipitation of metal hydroxides and carbonates using lime. Sludges associated with the secondary copper subcategory will necessarily contain additional quantities (and concentrations) of toxic metal pollutants. If a small excess of lime is added during treatment, the Agency does not believe these sludges would be identified as hazardous under RCRA in any case. (Compliance costs include this amount of lime.) Solid waste generation was considered for the promulgated 1975 BPT regulation; no additional solid waste generation is attributed to this regulation.

Although it is the Agency's view that solid waste generated as a result of these guidelines are not expected to be hazardous, generators of these wastes must test the waste to determine if the wastes meet any of the characteristics of hazardous waste (see 40 CFR 262.11).

If these wastes should be identified or are listed as hazardous, they will come within the scope of RCRA's "cradle to grave" hazardous waste management program, requiring regulation from the point of generation to point of final disposition. EPA's generator standards would require generators of hazardous nonferrous metals manufacturing wastes to meet containerization, labeling, record keeping, and reporting requirements; if plants dispose of hazardous wastes off-site, they would have to prepare a manifest which would track the movement of the wastes from the generators' premises to a permitted off-site treatment, storage, or disposal facility. See 40 CFR 262.20 45 FR 33142 (May 19, 1980), as amended at 45 FR 86973 (December 31, 1980). The transporter regulations require transporters of hazardous wastes to comply with the manifest system to assure that the wastes are delivered to a permitted facility. See 40 CFR 263.20 45 FR 33151 (May 19, 1980), as amended at 45 FR 86973 (December 31, 1980). Finally, RCRA regulations establish standards for hazardous waste treatment, storage, and disposal facilities allowed to receive such wastes. See 40 CFR Part 464 46 FR 2802 (January 12, 1981), 47 FR 32274 (July 26, 1982).

Even if these wastes are not identified as hazardous, they still must be disposed of in compliance with the Subtitle D open dumping standards, implementing 4004 of RCRA. See 44 FR 53438 (September 13, 1979). The Agency has calculated as part of the costs for wastewater treatment the cost of hauling and disposing of these wastes. For more details, see Section VIII of Vol. 1.

AIR POLLUTION

There is no reason to believe that any substantial air pollution problems will result from implementation of cooling towers and chemical precipitation and sedimentation. These technologies transfer pollutants to solid waste and are not likely to transfer pollutants to air.

TABLE VIII-1

COST OF COMPLIANCE FOR THE SECONDARY COPPER SUBCATEGORY

Indirect Dischargers
(March, 1980 Dollars)

Option	Capital Cost	Annual Cost
A	608432	270832
B	698498	277353

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

EPA promulgated BPT effluent limitations for the secondary copper subcategory on February 27, 1975 as Subpart F of 40 CFR Part 421. EPA is not promulgating any modifications to these limitations. With the exception of continuous rod casting, existing point sources may not discharge process wastewater pollutants to waters of the United States. Continuous copper rod casting performed at secondary copper plants is regulated under the metal molding and casting (foundries) point source category.

The zero discharge of process wastewater pollutants may be achieved by the application of lime precipitation, sedimentation, and filtration technology followed by the total recycle and reuse of treated water. The BPT effluent limitations include net precipitation and catastrophic storm allowances. A process wastewater impoundment which is designed, constructed and operated so as to contain the precipitation from the 10-year, 24-hour rainfall event as established by the National Climatic Center, National Oceanic and Atmospheric Administration, for the area in which such impoundment is located may discharge that volume of process wastewater which is equivalent to the volume of precipitation that falls within the impoundment in excess of that attributable to the 10-year, 24-hour rainfall event, when such event occurs. Also, during any calendar month there may be discharged from a process wastewater impoundment either a volume of process waste water equal to the difference between the precipitation for that month that falls within the impoundment and either the evaporation from the pond water surface area for that month, or a volume of process wastewater equal to the difference between the mean precipitation for that month that falls within the impoundment and the mean evaporation from the pond water surface area as established by the National Climatic Center, National Oceanic and Atmospheric Administration, for the area in which such impound is located (or as otherwise determined if no monthly data have been established by the National Climatic Center), whichever is greater.

The BPT limitations for the secondary copper subcategory continue:

Subject to the provisions of paragraphs (b), (c), and (d) of this section, there shall be no discharge of process wastewater pollutants into navigable waters.

(b) A process wastewater impoundment which is designed, constructed, and operated so as to contain the precipitation from the 10-year,24-hour rainfall event as established by the National Climatic Center, National Oceanographic and Atmospheric Administration, for the area in which such impoundment is located may discharge that volume of process wastewater equivalent to the volume precipitation that falls within the impoundment in excess of that attributable to the 10-year, 24-hour rainfall event, when such event occurs.

(c) During any calendar month there may be discharged from a process wastewater impoundment either a volume of process wastewater equal to the difference between the precipitation for the month that falls within the impoundment and either the evaporation from the pond water surface area for that month, or a volume of process wastewater equal to the difference between the mean precipitation for that month that falls within the impoundment and the mean evaporation from the pond water surface area as established by the National Climatic Center, National Oceanic and Atmospheric Administration, for the area in which such impoundment is located (or as otherwise determined if no monthly data have been established by the National Climatic Center), whichever is greater.

(d) Any process wastewater discharged pursuant to paragraph (c) of this section shall comply with each of the following requirements:

BPT Effluent Limitations

BPT Effluent Limitations	Maximum for any one day	Average of Daily Values for 30 Consecutive days shall not exceed
Pollutant or Pollutant Parameter	Metric Units (mg/l) English Units (ppm)	
Total Suspended Solids	50	25
Copper	0.5	0.25
Zinc	10	5
Oil and Grease	20	10
pH	Within the range of 6.0 to 9.0	

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

EPA promulgated BAT effluent limitations for the secondary copper subcategory on February 27, 1975 as Subpart F of 40 CFR Part 421. With the exception of continuous rod casting, these BAT effluent limitations prohibit the discharge of process wastewater pollutants into U.S. waters. Continuous copper rod casting is principally a copper forming or foundry operation because the copper is formed immediately after casting. Casting of products at copper forming facilities is regulated under the metal molding and casting (foundries) point source category. The zero discharge of process wastewater pollutants may be achieved by the application of lime precipitation, sedimentation and filtration technology followed by the total recycle and reuse of treated water. The BAT effluent limitations include the same net precipitation and catastrophic storm allowances as the existing BPT effluent limitations except the catastrophic storm is a 25-year, 24-hour rain fall event.

As discussed in Section IX of Vol. 1, the Agency is modifying its approach to stormwater. EPA is promulgating modifications to the 1975 BAT effluent limitations for the secondary copper subcategory to eliminate the net precipitation allowance. The impoundments used for cooling and settling process wastewater prior to recycle and reuse require much smaller surface areas than the settling evaporative impoundments for which the net precipitation discharge was allowed. Since cooling and settling impoundments have a much smaller surface area than evaporative impoundments, the net precipitation on these impoundments is small enough for secondary copper plants to accommodate. Costs for cooling towers were developed for BAT in the 1975 rulemaking when a plant had insufficient existing cooling impoundment capacity or cooling impoundments were not feasible due to space limitations. Thus, EPA is requiring that net precipitation on cooling and settling impoundments be used in secondary copper processes instead of being discharged. The promulgated BAT effluent limitations are, therefore, zero discharge of process wastewater pollutants to U.S. waters with allowances for the 25-year, 24-hour storm.

The promulgated BAT effluent limitations for the secondary copper Subcategory are as follows:

Subject to the provisions of paragraph (b) of this section, there shall be no discharge of process wastewater pollutants into navigable waters.

(b) A process wastewater impoundment which is designed, constructed, and operated so as to contain the precipitation from the 25-year,24-hour rainfall event as established by the National Climatic Center, National Oceanographic and Atmospheric

Administration, for the area in which such impoundment is located may discharge that volume of process wastewater equivalent to the volume precipitation that falls within the impoundment in excess of that attributable to the 25-year, 24-hour rainfall event, when such event occurs.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology (BDT). New plants have the opportunity to design the best and most efficient production processes and wastewater treatment technologies without facing the added costs and restrictions encountered in retrofitting an existing plant. Therefore, Congress directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible.

EPA is promulgating NSPS for the secondary copper subcategory as no discharge of process wastewater pollutants. EPA is also eliminating the allowance for catastrophic stormwater discharge provided at BAT. The Agency believes that new sources can be constructed with cooling towers exclusively, and that the cost of cooling towers instead of cooling impoundments is minimal. Some existing plants already use cooling towers rather than cooling impoundments, therefore, EPA believes that NSPS, as defined, does not constitute a barrier to entry for new plants.

SECTION XII

PRETREATMENT STANDARDS

INTRODUCTION

Section 307(b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES), which must be achieved within three years of promulgation. PSES are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of publicly-owned treatment works (POTW). The Clean Water Act of 1977 requires pretreatment for pollutants, such as toxic metals, that limit POTW sludge management alternatives. Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect discharge facilities, like new direct discharge facilities, have the opportunity to incorporate the best available demonstrated technologies, including process changes, in-plant controls, and end-of-pipe treatment technologies, and to use plant site selection to ensure adequate treatment system installation. Pretreatment standards are to be technology-based, analogous to the best available technology for removal of toxic pollutants.

EPA promulgated PSES for the secondary copper subcategory on December 15, 1976 as Subpart F of 40 CFR Part 421. The promulgated PSES allows a continuous discharge of process wastewater subject to specific limitations based on treatment with lime precipitation and sedimentation. Promulgated BAT (and promulgated BPT) for this subcategory require the zero discharge of process wastewater pollutants to U.S. waters. EPA is promulgating modifications to PSES to eliminate the disparity between BAT and PSES. Accordingly, EPA is promulgating PSES for the secondary copper subcategory equal to zero discharge of process waste water pollutants to POTW.

This section describes the control and treatment technologies for pretreatment of process wastewaters from existing sources and new sources in the secondary copper subcategory. Pretreatment standards for regulated pollutants are presented based on the selected treatment technology.

TECHNICAL APPROACH TO PRETREATMENT

Before promulgating pretreatment standards, the Agency examines whether the pollutants discharged by the industry pass through the POTW or interfere with the POTW operations or its chosen sludge disposal practices. In determining whether pollutants pass through a well-operated POTW, achieving secondary treatment, the Agency compares the percentage of a pollutant removed by POTW with the percentage removed by direct dischargers applying the best available technology economically achievable. A pollutant

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is deemed to pass through the POTW when the average percentage removed nationwide by well-operated POTW meeting secondary treatment requirements, is less than the percentage removed by direct dischargers complying with BAT effluent limitations guidelines for that pollutant. (See generally, 46 FR at 9415-16 (January 28, 1981).)

This definition of pass through satisfies two competing objectives set by Congress: (1) that standards for indirect dischargers be equivalent to standards for direct dischargers, while at the same time, (2) that the treatment capability and performance of the POTW be recognized and taken into account in regulating the discharge of pollutants from indirect dischargers.

The Agency compares percentage removal rather than the mass or concentration of pollutants discharged because the latter would not take into account the mass of pollutants discharged to the POTW from non-industrial sources nor the dilution of the pollutants in the POTW effluent to lower concentrations due to the addition of large amounts of non-industrial wastewater.

PRETREATMENT STANDARDS FOR EXISTING SOURCES

The treatment technologies considered for secondary copper plants discharging to POTW are:

Option A (Figure XII-1, page 1333) is based on:

- o Lime precipitation and sedimentation

Option G (Figure XII-2, page 1334) is based on:

- o Lime precipitation and sedimentation
- o In-process flow reduction with cooling towers and holding tanks
- o Total recycle and reuse of treated water

These two technology options for PSES are discussed in greater detail below. The first option considered (Option A) is identical to the technology basis for the existing PSES. The remaining option provides additional pollutant removal beyond that achieved by Option A.

Option A

Option A for the secondary copper subcategory is lime precipitation and sedimentation (lime and settle). Lime precipitation and sedimentation removes metals and suspended solids from process wastewater by the addition of lime followed by sedimentation.

Option G

Option G consists of the lime precipitation and sedimentation technology of Option A, followed by complete recycle and reuse of the treated water. In-process flow reduction measures consisting of the recycle of process wastewater through cooling towers or holding tanks is also added for Option G.

INDUSTRY COST AND POLLUTANT REMOVAL ESTIMATES

As one means of evaluating each technology option, EPA developed estimates of the pollutant removal and the compliance costs associated with each option. These methodologies are described below.

POLLUTANT REMOVAL ESTIMATES

A complete description of the methodology used to calculate the estimated pollutant reduction achieved by the application of the various treatment options is presented in Section X of vol. 1. The pollutant removal estimates have been revised from proposal based on comments and new data. The data used for estimating pollutant removals are the same as those used to revise the compliance costs. However, the methodology for calculating pollutant removals was not changed.

Sampling data collected during the field sampling program were used to characterize the major waste streams considered for regulation. At each sampled facility, the sampling data were production normalized for each unit operation (i.e., mass of pollutant generated per mass of product manufactured). This value, referred to as the raw waste, was used to estimate the mass of toxic pollutant generated within the secondary copper subcategory. By multiplying the total subcategory production for a unit operation times the corresponding raw waste value, the mass of pollutant generated for that unit operation was estimated.

The volume of wastewater discharged after the application of each treatment option was estimated for each operation at each plant by comparing the actual discharge to the regulatory flow. The smaller of the two values was selected and summed with the other plant flows. The mass of pollutant discharged was then estimated for each operation at each plant by comparing the actual discharge to the regulatory flow. The smaller of the two values was selected and summed with the other plant flows. The mass of pollutant discharged was then estimated by multiplying the achievable concentration values attainable by the option (mg/l) by the estimated volume of process wastewater discharged by the subcategory. The mass of pollutant removed is simply the difference between the estimated mass of pollutant generated within the subcategory and the mass of pollutant discharged after application of the treatment option. The pollutant removal estimates for indirect discharges in the secondary copper subcategory are presented in Table XII-1 (page 1332).

COMPLIANCE COSTS

Compliance costs presented at proposal (February 1983) were estimated using cost curves, which related the total costs associated with installation and operation of wastewater treatment technologies to plant process wastewater discharge. EPA applied these curves on a per plant basis, a plant's costs--both capital, and operating and maintenance--being determined by what treatment it has in place and by its individual process wastewater discharge (from dcp). The final step was to annualize the capital costs, and to sum the annualized capital costs, and the operating and maintenance costs, yielding the cost of compliance for the subcategory.

Since proposal, the cost estimation methodology has been changed as discussed in Section VIII of this document and in Section VIII of Vol. 1. A design model and plant specific information were used to size a wastewater treatment system for each discharging facility. After completion of the design, capital and annual costs were estimated for each unit of the wastewater treatment system. Capital costs rely on vendor quotes, while annual costs were developed from the literature. The revised compliance costs for indirect dischargers are presented in Table VIII-1 (page 1318).

PSES OPTION SELECTION

EPA has selected Option G as the basis for PSES. Option G consists of chemical precipitation and sedimentation, with cooling towers and holding tanks to achieve zero discharge of process wastewater pollutants. Implementation of Option G would remove an estimated 9,500 kg of toxic pollutants over estimated raw discharge. The estimated capital cost for achieving PSES is $654,000 (March, 1982 dollars), and the estimated annual cost is $277,000.

PSNS OPTION SELECTION

The technology basis for promulgated PSNS is identical to NSPS and BAT, which is zero discharge of all process wastewater pollutants (including no allowance for catastrophic stormwater discharges). PSNS does not increase costs compared to PSES or BAT, and EPA does not believe that PSNS will prevent the entry of new plants.

WASTEWATER DISCHARGE RATES

Specific wastewater streams associated with the secondary copper subcategory are residue concentration wastewater, slag granulation wastewater, reverberatory and rotary furnace wet air pollution control wastewater, spent electrolyte, scrap anode rinsing wastewater, casting contact cooling wastewater and casting wet air pollution control wastewater. None of these wastewater streams are allocated a discharge allowance for the promulgated PSES. The zero discharge requirement will eliminate the disparity between the 1976 PSES and the promulgated BAT effluent limitations. Each wastewater stream is discussed individually below.

RESIDUE CONCENTRATION

No discharge allowance is provided for residue concentration for PSES. Seven plants in the secondary copper subcategory generate residue concentration wastewater. The water use and discharge rates for residue concentration at these plants are shown in Table V-2 (page 1257). As shown in Table V-2, five of the seven plants practice total recycle and reuse of this waste stream, while only two plants discharge the residue concentration wastewater. The zero discharge of residue concentration wastewater is based on the five plants who do not discharge this wastewater.

SLAG GRANULATION

No discharge allowance is provided for slag granulation for PSES. Five plants in the secondary copper subcategory generate this waste stream. The water use and discharge rates for slag granulation at these plants are shown in Table V-3 (page 1258). As shown by Table V-3, all five plants practice total recycle and reuse of this waste stream. Accordingly, no discharge allowance is provided for slag granulation.

REVERBERATORY AND ROTARY FURNACE WET AIR POLLUTION CONTROL

No discharge allowance is provided for reverberatory and rotary furnace wet air pollution control for PSES. Five plants in the secondary copper subcategory use wet air pollution control on their rotary and reverberatory furnaces. The production normalized water use and discharge rates for reverberatory and rotary furnace wet air pollution control of these plants are shown in Table V-4 (page 1259). Three of the five plants completely recycle and reuse this waste stream. In addition, 13 plants control reverberatory and rotary furnace fumes and dust with dry air pollution control devices. Therefore, based on total recycle or dry air pollution control, no discharge allowance is provided for reverberatory and rotary furnace wet air pollution control.

SPENT ELECTROLYTE

No discharge allowance is provided for spent electrolyte for the PSES. Six plants in the secondary copper subcategory have an electrolyte refining process. The production normalized electrolyte use and discharge rates at these plants are shown in Table V-5 (page 1260). Four plants achieve zero discharge of spent electrolyte by either complete recycle (two plants) or by contract hauling (two plants). EPA believes that spent electrolyte is suitable for reuse in other plant operations after treatment consisting of cementation with iron (for copper recovery), lime precipitation, and sedimentation. For this reason, and since four of the six plants already achieve zero discharge for spent electrolyte, a discharge allowance is not provided.

SCRAP ANODE RINSING

No discharge allowance is provided for scrap anode rinsing for PSES. Two plants reported this waste stream. The water use and discharge rates for scrap anode rinsing at these plants are shown in Table V-6 (page 1261). Table V-6 shows that both of the plants with scrap anode rinsing practice 100 percent recycle. Accordingly, a discharge allowance is not provided for scrap anode rinsing.

CASTING CONTACT COOLING

With the exception of continuous rod casting, no discharge allowance is provided for casting contact cooling water. Continuous rod casting is principally a copper forming operation, and casting in this point source category is covered by the metal molding casting guidelines where continuous rod casting is given a discharge allowance. Twenty-two plants use casting contact cooling water in the secondary copper subcategory. The water use and discharge rates for casting contact cooling at these plants are shown in Table V-7 (page 1262). As shown in Table V-7, 10 of the 22 plants achieve zero discharge of this wastewater. EPA believes that the 12 plants which discharge this wastewater can also achieve zero discharge through recycle and reuse with cooling towers and holding tanks. Therefore, no discharge allowance is provided for casting contact cooling water.

CASTING WET AIR POLLUTION CONTROL

No discharge allowance is provided for casting wet air pollution control. Three plants in the secondary copper subcategory use wet air pollution control devices to control fumes from casting melting furnaces or pouring. The water use and discharge rates for casting wet air pollution control are shown in Table V-8 (page 1263). Table V-8 shows that one of the three plants completely recycle and reuses this waste stream. In addition, five plants use dry air pollution control devices to control fumes from casting operations. Therefore, based on total recycle or dry air pollution control, no discharge allowance is provided for casting wet air pollution control.

STORMWATER AND PRECIPITATION ALLOWANCES

No discharge allowance is provided for net precipitation stormwater for the promulgated PSES and PSNS. These standards are based on the use of cooling towers and holding tanks rather than cooling impoundments. Because cooling towers are not substantially affected by precipitation and the water using processes are water consuming, the balance between precipitation and evaporation should have no effect on the operability of the facility.

Catastrophic stormwater allowance is continued for PSES so that the requirements for direct dischargers meeting BAT and indirect dischargers meeting PSES are equivalent. Facilities using settling ponds to remove solids prior to recycle may need to discharge water after receiving water from a major precipitation event which exceeds their design parameters.

Because new plants have the opportunity to design to remove solids from wastewater using technologies that are not appreciably affected by rainfall, there is no catastrophic stormwater allowance provided for PSNS.

PRETREATMENT STANDARDS FOR EXISTING AND NEW SOURCES

EPA is promulgating a standard prohibiting the discharge of process wastewater pollutants for both PSES and PSNS for the secondary copper subcategory. The facility which discharges to a POTW will need to meet the same requirements as a facility discharging directly to the waters of the United States.

The pretreatment standard for an existing source (PSES) is:

(a) There shall be no discharge of process wastewater pollutants into a publicly owned treatment works subject to the provisions of paragraph (b) of this section.

(b) A process wastewater impoundment which is designed, constructed, and operated so as to contain the precipitation from the 25-year,24-hour rainfall event as established by the National Climatic Center, National Oceanographic and Atmospheric Administration, for the area in which such impoundment is located may discharge that volume of process wastewater equivalent to the volume precipitation that falls within the impoundment in excess of that attributable to the 25-year, 24-hour rainfall event, when such event occurs.

The pretreatment standard for a new source (PSNS) is:

There shall be discharge of process wastewater pollutants into a publicly owned treatment works.

TABLE XII-1

POLLUTANT REMOVAL ESTIMATES FOR SECONDARY COPPER INDIRECT DISCHARGERS

POLLUTANT	TOTAL RAW WASTE (kg/yr)	OPTION G DISCHARGED (kg/yr)	OPTION G REMOVED (kg/yr)
Arsenic	0.9	0.0	0.9
Cadmium	0.6	0.0	0.6
Chromium	18.1	0.0	18.1
Lead	286.6	0.0	286.6
Nickel	6,978.9	0.0	6,978.9
Selenium	0.0	0.0	0.0
Copper	1,680.1	0.0	1,680.1
Zinc	496.2	0.0	496.2
TOTAL TOXIC METALS	9,461.5	0.0	9,461.5
Aluminum	20.1	0.0	20.1
Ammonia	107.9	0.0	107.9
Fluoride	0.0	0.0	0.0
Iron	7,645.1	0.0	7,645.1
TOTAL NONCONVENTIONALS	7,773.1	0.0	7,773.1
TSS	3,358.8	0.0	3,358.8
Oil & Grease	720.9	0.0	720.9
TOTAL CONVENTIONALS	4,079.6	0.0	4,079.6
TOTAL POLLUTANTS	21,314.2	0.0	21,314.2
FLOW (l/yr)		0	

NOTE: TOTAL TOXIC METALS = Arsenic + Cadmium + Chromium + Lead + Nickel + Selenium + Copper + Zinc
TOTAL NONCONVENTIONALS = Aluminum + Ammonia + Fluoride + Iron
TOTAL CONVENTIONALS = TSS + Oil & Grease
TOTAL POLLUTANTS = Total Toxic Metals + Total Nonconventionals + Total Conventionals

OPTION G = In-Process Flow Reduction, Lime Precipitation and Sedimentation followed by complete recycle or reuse of treated water.

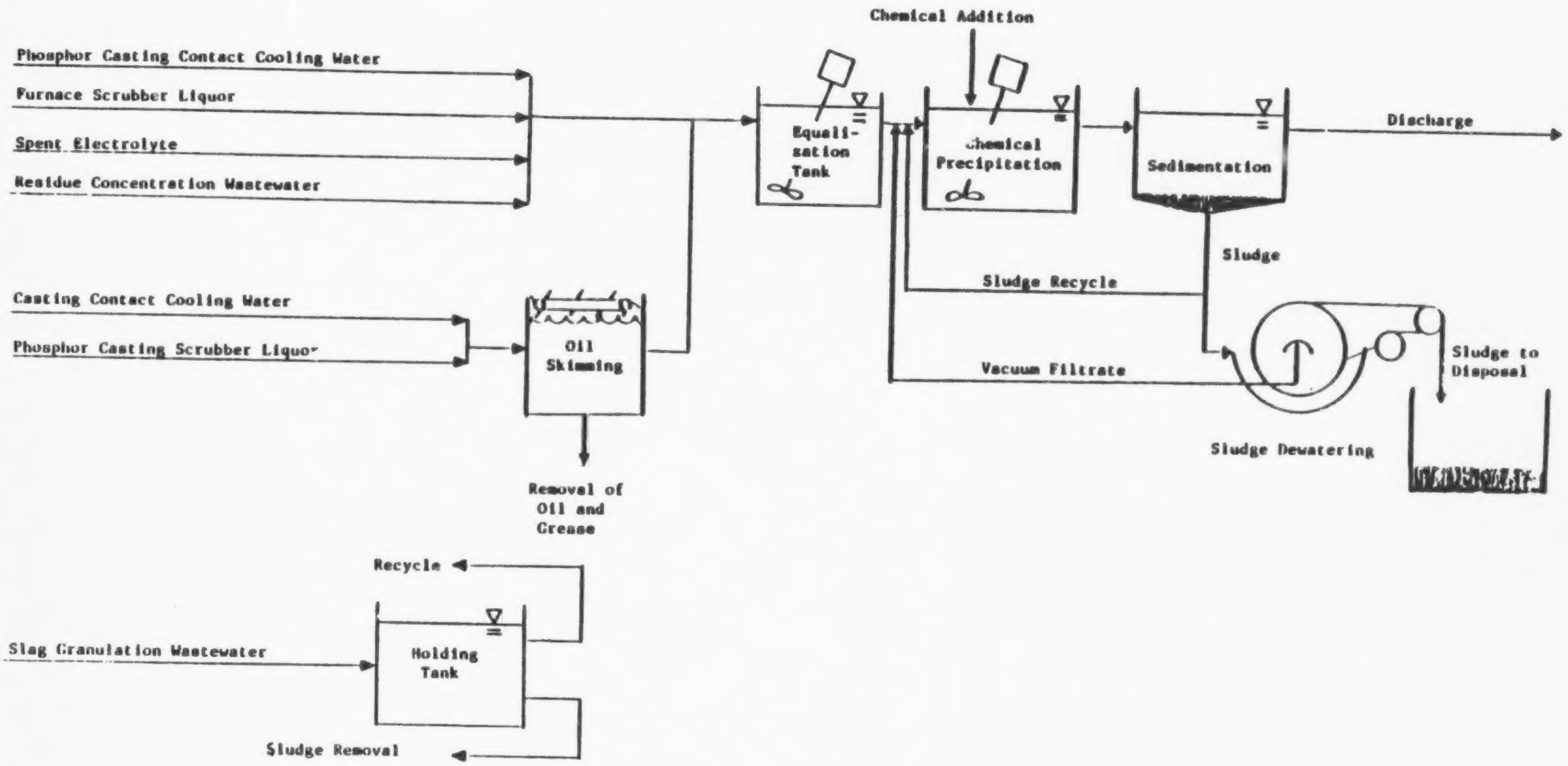
Phosphor Casting Contact Cooling Water
Furnace Scrubber Liquor
Spent Electrolyte
Residue Concentration Wastewater
Casting Contact Cooling Water
Phosphor Casting Scrubber Liquor
Oil Skimming
Removal of Oil and Grease
Equalization Tank
Chemical Addition
Chemical Precipitation
Sedimentation
Discharge
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge Dewatering
Sludge to Disposal
Recycle
Slag Granulation Wastewater
Holding Tank
Sludge Removal

Figure XII-1

PSES TREATMENT SCHEME OPTION A
SECONDARY COPPER SUBCATEGORY

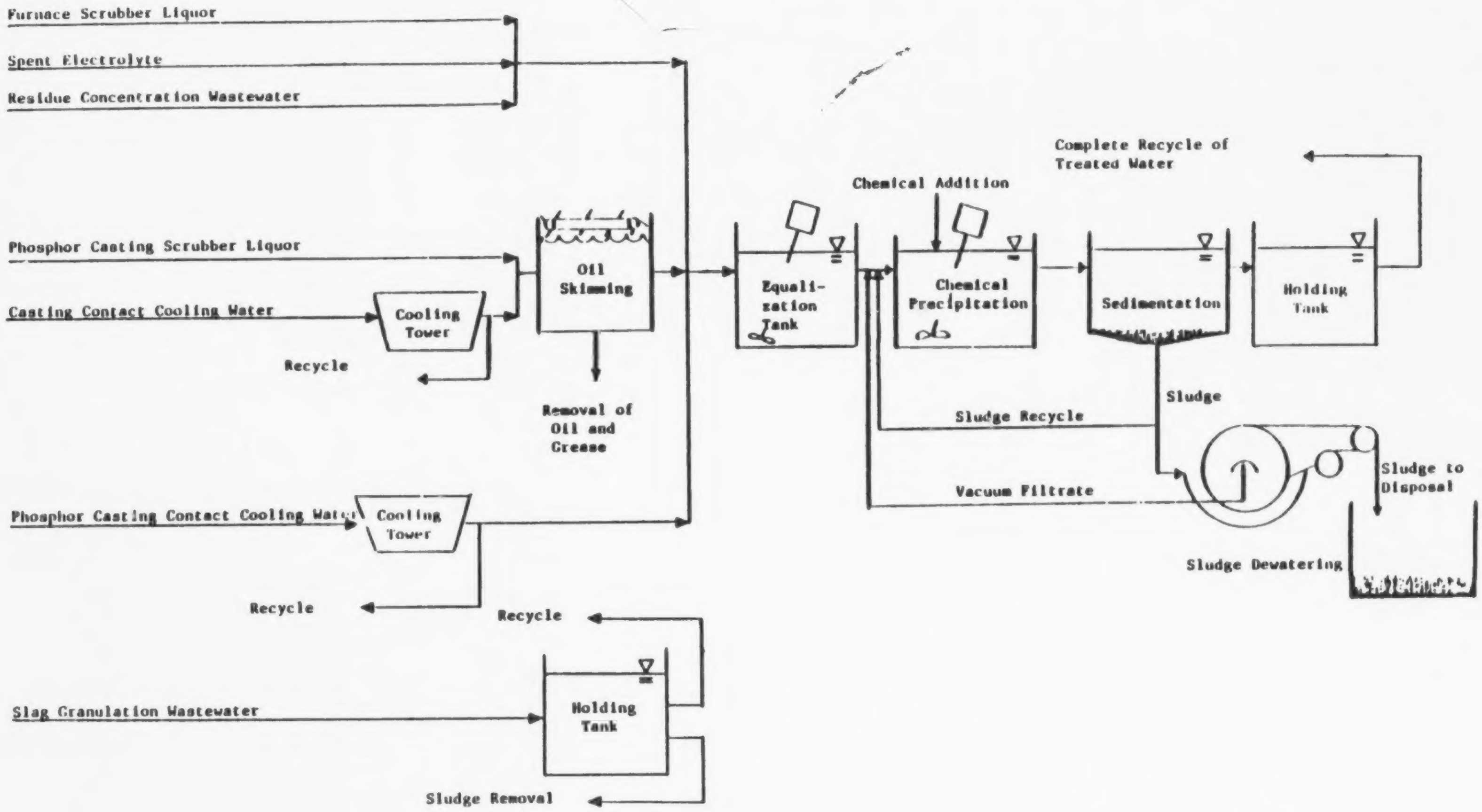
Furnace Scrubber Liquor
Spent Electrolyte
Residue Concentration Wastewater
Phosphor Casting Scrubber Liquor
Casting Contact Cooling Water
Cooling Tower
Recycle
Oil Skimming
Removal of Oil and Grease
Phosphor Casting Contact Cooling Water
Cooling Tower
Recycle
Recycle
Slag Granulation Wastewater
Holding Tank
Sludge Removal
Equalization Tank
Chemical Addition
Chemical Precipitation
Complete Recycle of Treated Water
Sedimentation
Holding Tank
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge to Disposal
Sludge Dewatering

Figure XII-2

PSES TREATMENT SCHEME OPTION G
SECONDARY COPPER SUBCATEGORY

SECTION XIII

BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY

EPA is not promulgating best conventional pollutant control technology (BCT) for the secondary copper subcategory at this time.

NONFERROUS METALS MANUFACTURING POINT SOURCE CATEGORY

DEVELOPMENT DOCUMENT SUPPLEMENT

for the

Metallurgical Acid Plants Subcategory

William K. Reilly
Administrator

Rebecca Hanmer
Acting Assistant Administrator for Water

Martha Prothro, Director
Office of Water Regulations and Standards

Thomas P. O'Farrell, Director
Industrial Technology Division

Ernst P. Hall, P.E., Chief
Metals Industry Branch
and
Technical Project Officer

May 1989

U.S. Environmental Protection Agency
Office of Water
Office of Water Regulations and Standards
Industrial Technology Division
Washington, D. C. 20460

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METALLURGICAL ACID PLANT SUBCATEGORY

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SECTION I

SUMMARY

On April 8, 1974, EPA promulgated technology-based effluent limitations and standards for several subcategories of the Nonferrous Metals Manufacturing Point Source Category. This regulation included BPT, BAT, NSPS, and PSNS limitations.

EPA promulgated technology-based effluent limitations for the metallurgical acid plant subcategory of the Nonferrous Metals Manufacturing Point Source Category on July 2, 1980 (45 FR 44926). Best practicable control technology currently available (BPT) effluent limitations were established. This new subcategory covered all operations associated with the manufacture of by-product sulfuric acid at primary copper plants and included associated air pollution control (or gas conditioning systems) for sulfur dioxide off-gases from pyrometallurgical operations.

On March 8, 1984 (49 FR 8742), EPA expanded the metallurgical acid plant subcategory and established BAT, NSPS, PSES, and PSNS pursuant to the provisions of Sections 301, 304, 306 and 307 of the Clean Water Act, as amended. EPA expanded this subcategory to include analogous operations associated with the manufacture of by-product sulfuric acid from primary lead and primary zinc plants. On September 20, 1985 (50 FR 38276) the metallurgical acid plants subcategory was further expanded to include by-product sulfuric acid plants associated with primary molybdenum roasting operations. The pollutants regulated at BPT, BAT, NSPS and PSNS were revised to take into account pollutants specific to primary molybdenum acid plants by adding the pollutants molybdenum and fluoride to the regulated pollutants for molybdenum acid plants only, however, PSES was not revised because there are no indirect discharging primary molybdenum acid plants. This supplement provides a compilation and analysis of the background material used to develop these effluent limitations and standards.

EPA entered into a settlement agreement in June 1987, with AMAX, Inc., and GTE Products Corp., two petitioners affected by the regulations for the Metallurgical Acid Plants Subcategory. This Settlement Agreement concerns one topic, molybdenum limitations, which is briefly described here, and more fully described elsewhere in this document. The molybdenum limitations were suspended until petitioners install the model technology, iron coprecipitation, and submit data to the Agency. EPA agreed to recommend two sets of interim limits to permit writers. The first set of interim limits would be based on a monthly average treatment effectiveness of 30 mg/l and a daily maximum of 60 mg/l and will be effective until April 30, 1988. At that time, if no full-scale data are available, the second set of interim limits will be based on the results of bench-scale iron coprecipitation data obtained under the supervision of the Agency.

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The metallurgical acid plant subcategory is comprised of 22 facilities. Of the 22 plants, 10 discharge directly to rivers, lakes, or streams; two discharge to a publicly owned treatment works (POTW); and 10 achieve zero discharge of process wastewater.

EPA first studied the metallurgical acid plant subcategory to determine whether differences in raw materials, final products, manufacturing processes, equipment, age and size of plants, water usage, required the development of separate effluent limitations and standards for different segments of the subcategory. This involved a detailed analysis of wastewater discharge and treated effluent characteristics, including (1) the sources and volume of water used, the processes used and the sources of pollutants and wastewaters in the plant; and (2) the constituents of waste waters, including toxic pollutants.

EPA also identified several distinct control and treatment technologies (both in-plant and end-of-pipe) applicable to the metallurgical acid plant subcategory. The Agency analyzed both historical and newly generated data on the performance of these technologies, including their nonwater quality environmental impacts (such as air quality impacts or solid waste generation) and energy requirements. EPA also studied various flow reduction techniques reported in the data collection portfolios (dcp) and plant visits.

Engineering costs were prepared for each of the control and treatment options considered for the category. These costs were then used by the Agency to estimate the impact of implementing the various options on the industry. For each control and treatment option that the Agency found to be most effective and technically feasible in controlling the discharge of pollutants, the number of potential closures, number of employees affected, and impact on price were estimated. These results are reported in a separate document entitled Economic Impact Analysis of Effluent Limitations and Standards for the Nonferrous Metals Smelting and Refining Industry.

Based on consideration of the above factors, EPA identified various control and treatment technologies which formed the basis for BAT and selected control and treatment appropriate for each set of limitations and standards. The mass limitations and standards for BAT, NSPS, PSES, and PSNS are presented in Section II.

For BAT, the Agency has built upon the BPT basis of lime precipitation and sedimentation by adding in-process control technologies which include recycle of process water from air pollution control and metal contact cooling wastewater streams. Sulfide precipitation may also be a necessary treatment step at various facilities. Iron co-precipitation may be necessary for primary molybdenum acid plants in order to achieve the limitations for molybdenum. Filtration is added as an effluent polishing step to the end-of-pipe treatment scheme. To meet the BAT effluent limitations based on this technology, the metallurgical acid plant subcategory is estimated to incur a capital cost of $2.5 million (1982 dollars) and an annual cost of $2.0 million (1982 dollars).

The best demonstrated technology (BDT), which is the technical basis of NSPS, is equivalent to BAT. In selecting BDT, EPA recognizes that new plants have the opportunity to implement the best and most efficient manufacturing processes and treatment technology. As such, the technology basis of BAT has been determined as the best demonstrated technology.

The Agency is promulgating pretreatment standards for existing sources (PSES) equal to BAT. To meet the PSES, the metallurgical acid plant subcategory is estimated to incur a capital cost of $0.161 million (1982 dollars) and an annual cost of $0.085 million (1982 dollars). The technology basis for pretreatment standards for new sources (PSNS) is the best demonstrated technology, which is BAT. As such, the PSNS are identical to NSPS for all waste streams.

SECTION II

CONCLUSIONS

EPA has not divided the metallurgical acid plant subcategory into segments for the purpose of effluent limitations and standards. This single building block is referred to as acid plant blowdown and generally includes wastewater generated through wet scrubbing and humidification to precondition gases before they enter an acid plant along with the acid plant wastewater which is mostly generated by eliminating entrained mist before the gas is discharged to the atmosphere.

EPA promulgated BPT effluent limitations for the metallurgical acid plants subcategory on July 2, 1980 (45 FR 44926) as Subpart I of 40 CFR Part 421. These BPT effluent limitations apply to process wastewater discharges resulting from or associated with the manufacture of by-product sulfuric acid at primary copper smelters, including any associated air pollution control or gas-conditioning systems for sulfur dioxide off-gases from pyrometallurgical operations. On March 8, 1984 (49 FR 8742), EPA expanded the metallurgical acid plants subcategory to include sulfuric acid plants at primary lead and primary zinc plants. On September 20, 1985 (50 FR 38276) EPA further expanded the metallurgical acid plants subcategory to include metallurgical acid plants at primary molybdenum facilities. The pollutants molybdenum and fluoride are regulated for primary molybdenum acid plants only. Presented below are the BPT effluent limitations for the metallurgical acid plants subcategory.

BPT EFFLUENT LIMITATIONS

Pollutant or Pollutant Property	Maximum For Any One Day	Maximum For Monthly Average
mg/kg (lb/million lbs) of 100 percent sulfuric acid capacity		
Cadmium	0.180	0.090
Copper	5.000	2.000
Lead	1.800	0.790
Zinc	3.600	0.900
Fluoride[1]	212.800	121.000
Molybdenum[1]	Reserved	Reserved
Total Suspended Solids	304.000	152.000
pH	Within the range of 6.0 to 9.0	

[1] For molybdenum acid plants only.

BAT is promulgated based on the performance achievable by the application of chemical precipitation, sedimentation, and

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multimedia filtration (lime, settle, and filter) technology and in-process flow reduction control methods. Sulfide precipitation is added at various facilities to achieve the performance of lime, settle, and filter technology. Iron co-precipitation is added for acid plants associated with primary molybdenum roasting operations in order to control discharges of molybdenum. The following BAT effluent limitations are promulgated for existing sources:

(a) Acid Plant Blowdown

BAT EFFLUENT LIMITATIONS

Pollutant or Pollutant Property	Maximum For Any One Day	Maximum For Monthly Average
mg/kg (lbs/million lbs) of 100 percent sulfuric acid capacity		
Arsenic	3.550	1.584
Cadmium	0.511	0.204
Copper	3.269	1.558
Lead	0.715	0.332
Zinc	2.605	1.073
Fluoride[1]	89.390	50.820
Molybdenum[1]	Reserved	Reserved

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[1] For molybdenum acid plants only.

NSPS are promulgated based on the performance achievable by the application of chemical precipitation, sedimentation, and multimedia filtration (lime, settle, and filter) technology and in-process flow reduction control methods. Sulfide precipitation is added at various facilities to achieve the performance of lime, settle, and filter technology. Iron co-precipitation is added for acid plants associated with primary molybdenum roasting operations to achieve the effluent standards for molybdenum. The following effluent standards are promulgated for new sources:

(a) Acid Plant Blowdown NSPS

Pollutant or Pollutant Property	Maximum For Any One Day	Maximum For Monthly Average
mg/kg (lbs/million lbs) of 100 percent sulfuric acid capacity		
Arsenic	3.550	1.584
Cadmium	0.511	0.204
Copper	3.269	1.558
Lead	0.715	0.332
Zinc	2.605	1.073
Fluoride[1]	89.390	50.820
Molybdenum[1]	Reserved	Reserved
TSS	38.310	30.650
pH	Within the range of 7.5 to 10.0 at all times	

[1] For molybdenum acid plants only.

PSES are promulgated based on the performance achievable by the application of chemical precipitation, sedimentation, and multimedia filtration (lime, settle, and filter) technology and in-process flow reduction control methods. Sulfide precipitation is added at various facilities to achieve the performance of lime, settle, and filter technology. The following pretreatment standards are promulgated for existing sources:

(a) Acid Plant Blowdown PSES

Pollutant or Pollutant Property	Maximum For Any One Day	Maximum For Monthly Average
mg/kg (lbs/million lbs) of 100 percent sulfuric acid capacity		
Cadmium	0.511	0.204
Zinc	2.605	1.073

PSNS are promulgated based on the performance achievable by the application of chemical precipitation, sedimentation, and multimedia filtration (lime, settle, and filter) technology and in-process flow reduction control methods. Sulfide precipitation is added at various facilities to achieve the performance of lime, settle, and filter technology. Iron co-precipitation is added for acid plants associated with primary molybdenum roasting operations in order to control discharges of molybdenum. The following pretreatment standards are promulgated for new sources:

(a) Acid Plant Blowdown PSNS

Pollutant or Pollutant Property	Maximum For Any One Day	Maximum For Monthly Average
mg/kg (lbs/million lbs) of 100 percent sulfuric acid capacity		
Arsenic	3.550	1.584
Cadmium	0.511	0.204
Copper	3.269	1.558
Lead	0.715	0.332
Zinc	2.605	1.073
Fluoride[1]	89.390	50.820
Molybdenum[1]	Reserved	Reserved

---

[1] For molybdenum acid plants only.

SECTION III

SUBCATEGORY PROFILE

This section introduces the raw materials and processes used in the production of sulfuric acid from SO_2 off-gases from primary copper, lead, molybdenum, and zinc plants, and presents a profile of the acid plants identified in this study.

DESCRIPTION OF METALLURGICAL ACID PLANTS

Metallurgical acid plants produce sulfuric acid from the emissions of pyrometallurgical operations. By producing acid, the acid plants not only clean the smelter emissions of many tons per day of sulfur oxides, but they also produce a marketable sulfuric acid product.

This section describes the metallurgical acid plant processes and the steps which may be required to pretreat the gas. These processes are shown in Figure III-1 (page 1361). An acid plant catalytically converts sulfur dioxide in a smelter off-gas stream to sulfur trioxide, and then absorbs it into a sulfuric acid stream. The sulfur trioxide combines with the water in the absorbing sulfuric acid which, in effect, increases the strength of the contacting acid stream. Prior to entering the acid plant, the smelter off-gas stream will usually undergo one or more pretreatment steps.

RAW MATERIALS

Primary copper, lead, molybdenum, and zinc are predominantly produced from sulfide ore concentrates. In the various pyrometallurgical operations used to produce these metals, large amounts of sulfur oxides are evolved. Air pollution regulations affecting smelters, in the form of State Implementation Plans (SIP), as well as federal new source performance standards, set limits on the mass of SO_2 discharged. In order to meet these limits, SO_2 is removed from the smelter off-gases often resulting in installation of permanent SO_2 controls at primary metals plants such as metallurgical acid plants.

As used in this supplement, "acid plant" also includes plants producing elemental sulfur and liquid SO_2, since these operations use similar conditioning and cleaning prior to production of the sulfur-containing product. These products are produced using the same raw material (high-sulfur-content emissions) as a sulfuric acid plant. This section will discuss the origin of the sulfur oxides in the production sequence for each metal.

Copper

The most important type of copper ore in the United States is mined from the "porphyry" copper deposits. These low-grade deposits are extensive masses of rock containing crystals of various copper minerals which may be profitably mined on a massive, non-selective scale. Copper minerals generally associated with the porphyrys are various oxides, such as cuprite and malachite, which have been formed from parent minerals near the surface of a deposit through weathering processes. Deeper in a deposit, various sulfide minerals, such as chalcocite, covellite. and chalcopyrite, typically occur. Porphyry ores are mined by open pit methods. Other major types of deposits are vein, pipe, and bedded deposits, which yield higher grade ores and are usually mined using underground methods. Copper minerals in these deposits commonly include chalcopyrite, bornite, chalcocite, and covellite. A few American deposits are deep seated and contain some copper-arsenic minerals, such as enargite. Native copper is only found in important quantities in Michigan, where it is found in conjunction with covellite. The compositions of the more important copper minerals are shown below.

Mineral	Composition
Bornite	Cu_5FeS_4
Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$
Covellite	CuS
Cuprite	Cu_2O
Enargite	$Cu_3As_5S_4$
Malachire	$CuCO_3 \cdot Cu(OH)12s$
Native Copper	Cu

Oxides of sulfur are released during the principal pyrometallurgical operations at primary copper smelters. If roasting is practiced at the smelter, about 25 percent of the sulfur in the feed will be converted to sulfur oxides, principally sulfur dioxide; 25 percent will be oxidized during smelting in the reverberatory or electric furnace; and the remaining 50 percent will evolve from the converting operation. At smelters which do not use roasters, about 40 percent of the sulfur in the feed is oxidized during smelting in the reverberatory furnace, and the remaining 60 percent is evolved during converting.

The sulfur dioxide concentration in roaster and converter off-gases can be maintained between 4 and 14 percent by volume, providing that leaks of infiltrating air into the flues are minimized and good operating practices are followed.

The SO_2 concentration in roaster off-gases can be high enough (5 percent SO_2 in new hearth roaster gases, and 8 to 10 percent SO_2 in fluid bed roaster gases) to permit sulfuric acid manu-facture. However, older hearth roaster systems produce a lower concentration in the off-gases because of infiltrating air. Typical concentrations are about 1.0 to 2.5 percent.

Roasted concentrates are charged to a smelting furnace where fluxing agents are added. Iron present in the charge reacts with the fluxing agents forming an iron silicate slag. The slag is skimmed from the top of the reverberatory furnace leaving a white metal about 70 percent copper and 24 percent sulfur. Gaseous emissions from the reverberatory furnace contain an average of 0.4 to 1.5 percent SO_2, too low for direct processing in a sulfuric acid plant.

Copper matte tapped from the bottom of the smelting furnace is charged to a converter for further purification. In the converter, compressed air is blown through the copper to oxidize impurities including sulfur. This is known as the slag blow which produces average off-gas SO_2 concentrations of 10 percent. When collected by the primary converter hood, this value will be diluted to an average of 5 percent. Further blowing converts most of the remaining sulfur to SO_2, leaving a final blister copper usually containing between 98.5 and 99.3 percent copper, 0.3 percent sulfur, some dissolved oxygen, and other impurities.

Lead

The major lead mineral is galena, PbS, which is commonly associated with cerussite ($PbCO_3$) and anglesite ($PbSO_4$), both of which result from weathering of galena. Typical lead concentrates range from 45 to 80 percent lead, with 10 to 30 percent sulfur, as well as traces of other metals and contaminants. The concentrated ore is sintered so that it can be used in the blast furnace. The majority of the sulfur contained in the feed concentrate is converted to SO_2 in the front portion of the sintering machine. This gas stream may be segregated from the weaker (lower SO_2 concentration) off-gases from the rear section of the sintering machine. Some plants collect all the sinter machine off-gases in one flue, and they are emitted after only particulate control. These plants, which have no acid plant, are not included in this subcategory.

Molybdenum

The primary source of molybdenum is a molybdenum sulfide ore called molybdenite (MoS_2). Most domestic molybdenite is mined and concentrated at two large mines in Colorado and a smaller amount comes from a mine in New Mexico. Molybdenite is also recovered as a by-product from concentrating porphyry copper ores. Molybdenum sulfide is converted to technical grade molybdic oxide, MoO_3, in multiple hearth furnaces. The temperature must be controlled to ensure complete oxidation of all sulfur and to limit losses due to volatilization of MoO_3 which becomes significant at 1,300°F. Molybdenite roaster off-gases may contain fluoride in addition to SO_2. Fluoride is removed from the feed gas in a water scrubber prior to sulfuric acid production.

Zinc

The most important zinc mineral is sphalerite, ZnS. Some zinc deposits contain oxide, carbonate, or silicate zinc minerals. Often, zinc is found in the same or adjacent deposits with lead. In such an occurrence, it is separated from the lead ores in the concentrator. Since zinc sulfide is insoluble in the sulfuric acid used for leaching at electrolytic plants, the sulfide ore concentrates are roasted as completely as possible to form zinc oxide and sulfur oxide. Roasting may take place in a multiple hearth, fluid bed, or flash roaster. Concentrations of SO_2 in the off-gas vary with the type of roaster used. In a multiple hearth roaster, the concentration ranges from about 4.5 to 6.5 percent SO_2. Off-gas from a suspension roaster has a higher SO_2 concentration, averaging 10 to 13 percent. SO_2 concentrations in the off-gas from a fluidized bed roaster range from 7 to 12 percent, although the higher figure is more common. A fluid column roaster averages 11 to 12 percent SO_2 in the flue gas.

APPLICABILITY OF METALLURGICAL ACID PLANTS

The applicability of metallurgical acid plants for controlling smelting off-gases is dependent upon the SO_2 concentrations in the off-gases. Pyrometallurgical processes used in the production of copper, lead, molybdenum, and zinc from sulfide ores release SO_2 to the off-gas systems at concentrations ranging from less than 1 percent to over 10 percent.

Sulfuric acid plants are usually designed for an SO_2 concentration of 4 to 10 percent with any higher concentrations being diluted with air. Elemental sulfur and liquid SO_2 plants are favored for highly concentrated SO_2 streams (e.g., 80 percent). Since the SO_2 concentrations in copper, lead, molybdenum, and zinc plant off-gases are generally in the 1 to 10 percent range, most of these plants produce sulfuric acid as the by-product of SO_2 control.

Modern smelting processes, such as electric furnaces, oxygen enrichment, flash smelting, and continuous smelting produce off-gases with higher SO_2 concentrations than many of the older processes. For example, reverberatory furnace gases from conventional equipment usually contain 0.5 to 2 percent SO_2. For the same amount of SO_2 per hour, the more concentrated the gas stream is, the cheaper the acid plant is to build and operate. Because of this, some of the new smelter processes producing gas streams with high SO_2 concentrations, such as the Outokumpu flash smelter or the Mitsubishi process, offer significant advantages. The addition of oxygen to the smelting operation can result in more highly concentrated SO_2 off-gases. Some of these newer processes, such as the Mitsubishi process, also have the advantage that the gases from all the furnaces (smelting, slag cleaning, and converting) can be combined to produce a single gas stream with an SO_2 concentration which still permits acid production.

PROCESS DESCRIPTION

The process descriptions which follow concentrate on water uses and wastewater sources in the acid plant and pretreatment equipment. Each of the various water and wastewater streams discussed are present in some or all acid plants. The existence of any specific waste stream in a particular plant depends on the specific plant design. These wastewater streams are usually combined and treated as a single stream, termed "acid plant blowdown."

The following discussion provides more detailed information on acid plant processes shown in Figure III-1 (page 1362).

Cooling

The temperature of the gas from the pyrometallurgical operation may be in the range of 400 to 1,200°F, depending upon the specific operation. Typically, zinc roasters operate around 1,200°F, while the gas exiting a copper converter is about 500°F, and that from a lead sintering machine is around 800°F. Molybdenum roasters operate at approximately 900-1,100°F.

Gases from a zinc fluid bed roaster may be sprayed with water from the dome of the roaster to humidify and cool the gas. A waste heat boiler may be used, which produces usable steam and cools the gas stream at the same time. The gases may go through a humidification chamber, which reduces the temperature and partially humidifies the gas. The gas is cooled to some extent by radiation in the ductwork. No wastewater stream is produced in this cooling step since all the water added is evaporated.

Cleaning

Cleaning is performed to remove particulate matter which may catalyze undesirable side reactions downstream. Various methods are used to clean the acid plant feed gas, such as electrostatic precipitators, baghouses, cyclones, multiple cyclones, wet scrubbers, and settling chambers. The most common method is electrostatic precipitators.

Conditioning

In order to produce sulfuric acid of the desired strength, water vapor must be present in a precise ratio of water to SO_2. Production of 93 percent acid requires about a 1.4 mole ratio of water to SO_2, while 100 percent acid requires a 1.0 mole ratio. The conditioning or humidification step adds a slight excess of water to the gas, and the excess is then condensed out. Open and packed towers or various types of scrubbers may be used for this process step. Scrubbers are often used in conjunction with a gas cooling tower to condense the excess water.

This phase of the process serves several purposes: the gas is further cooled, more of the dust and particulates are removed, and the gas is humidified to the proper degree. Since SO_3 in contact with water forms H_2SO_4, the scrubbing liquor becomes a weak acid, which is usually recirculated with a blowdown (acid plant scrubber blowdown). A scrubber makeup water stream is also required.

Mist Precipitation

The gas leaving the conditioning process unit contains acid mist, as well as particulate matter. This is usually removed in an electrostatic precipitator, called a mist precipitator. These units operate at efficiencies of over 98 percent and produce an acidic wastewater containing toxic metals (mist precipitator blowdown).

Drying

Drying towers remove entrained moisture by contact with sulfuric acid (93 to 98 weight percent). Usually an absorber acid recycle stream (from the downstream acid production section) is used for this drying step. The absorbing acid stream becomes slightly diluted with water during this step. This removed water later contacts SO_3 in the absorber to form sulfuric acid.

Compression

A blower may be required to boost the gas pressure prior to entering the acid production section of the plant. As the pressure of the gas stream is increased, water vapor is condensed and collected as a wastewater.

A bearing cooling wastewater stream may be produced in this step if once-through cooling water is used. This waste stream, however, is considered nonscope for this regulation and must be handled on a case-by-case basis by the permit writer.

Acid Production

In the acid production section, the gas containing SO_2 contacts a vanadium pentoxide catalyst, and the gas is catalytically oxidized to SO_3. The sulfur trioxide is then absorbed in 98 percent acid, which becomes more concentrated. Dilute sulfuric acid or water is added to the recirculating acid, and excess acid is withdrawn from the system. Oleum (a mixture of H_2SO_4 and free SO_3) may also be produced by absorbing the SO_3 in 98 percent acid. In oleum production, less water or dilute sulfuric acid is used to contact the gas, leaving some SO_2 unconverted. Oleum typically contains 20 percent SO_3 and 80 percent of 100 percent H_2SO_4. The acid plant tail gas contains about 2,000 to 3,000 ppm SO_2 by volume and some entrained acid mist.

Many sulfuric acid plants must meet an SO_2 discharge concentration limitation which cannot be met by single-contact acid plants. In many acid plants the gas stream leaving the absorber is returned to the converter for oxidation of additional

SO_2 to SO_3. The resultant gas stream then flows to a second absorption tower (not shown in Figure III-1) and is contacted with 98 percent acid These double-contact acid plants can produce a final SO_2 concentration in the tail gas of less than 200 ppmv. About half of the metallurgical acid plants in the U.S. are of the double-contact type. Since the S03 formed in the first contacting step has been absorbed, the second contacting favors more complete oxidation of SO_2 than is possible with single contacting. Overall conversion is on the order of 99.8 percent, rather than the 95.5 to 98.5 conversion achieved in a single-contact acid plant.

The off-gas from the final absorption tower flows to a mist eliminator and then is discharged to the atmosphere through a stack.

The potential water uses and wastewater sources in metallurgical acid plants are indicated in Figure III-1. The block diagram shown in Figure III-1 is of a typical metallurgical acid plant.

Other gas conditioning, gas cooling, gas cleaning, etc. technologies may be used instead of or in addition to the ones shown. Therefore the water uses and wastewater sources shown are also representations of typical streams, and their occurrences are functions of the processing equipment in each acid plant.

PROCESS WASTEWATER SOURCES

The principal wastewater sources in the metallurgical acid plants subcategory are as follows:

1. Acid plant scrubber blowdown,
2. Mist precipitator blowdown,
3. Compression condensate,
4. Box cooler blowdown, and
5. Mist eliminator blowdown.

These wastewater sources have been combined into the single wastewater stream, acid plant blowdown.

OTHER WASTEWATER SOURCES

There are other wastewater streams associated with the metallurgical acid plants subcategory. These waste streams may include bearing cooling water return, steam generator blowdown, maintenance and cleanup water, and stormwater runoff. These wastewater streams are not considered as a part of this rulemaking. EPA believes that the flows and pollutant loadings associated with these waste streams are insignificant relative to the wastewater streams selected and are best handled by the appropriate permit issuing authority on a case-by-case basis.

AGE, PRODUCTION, AND PROCESS PROFILE

There are 22 metallurgical acid plants in the United States, as shown in Figure III-2 (page 1363). Ten sulfuric acid plants are at primary copper plants, three are at primary lead plants, three are at primary molybdenum plants, and six are at primary zinc plants. All but one of the plants associated with copper production are located in Texas or west of Texas. All except for one of these are zero discharge acid plants. Two of the plants associated with lead are located in Missouri and both are direct discharge plants. The other is a zero discharge plant and is located in Montana. Of the three sulfuric acid plants associated with molybdenum roasting operations, two are in Pennsylvania and one is in Iowa. One achieves zero discharge of process wastewater and two are direct dischargers. The six zinc-related acid plants are located between Texas and Pennsylvania. Four are direct dischargers and two are indirect dischargers. Table III-1 (page 1361) shows the number of acid plants associated with copper, lead, molybdenum and zinc, and the discharge status of these plants.

There are insufficient data to ascertain the age of acid plants independently of the base metal plants associated with them. Acid plants are a result of air pollution abatement measures at existing metal production facilities. Acid plants, due to corrosive products and materials, have relatively short life spans. Periodically the acid plant is taken off-line for maintenance and upkeep. The frequency of maintenance is dependent on individual plant operating procedures.

Table III-2 (page 1361) shows that the acid production range figures for these plants are fairly evenly distributed among all categories with acid productions up to 300,000 kkg per year.

All acid plants that provided dcp information use water, and all but one of these plants generate an acid plant blowdown stream. In the plant that does not generate a blowdown stream, the water is evaporated (in-process) during cooling of the smelter off-gas stream. Other acid plants, through reuse and evaporation practices, may generate but not discharge acid plant blowdown.

TABLE III-1

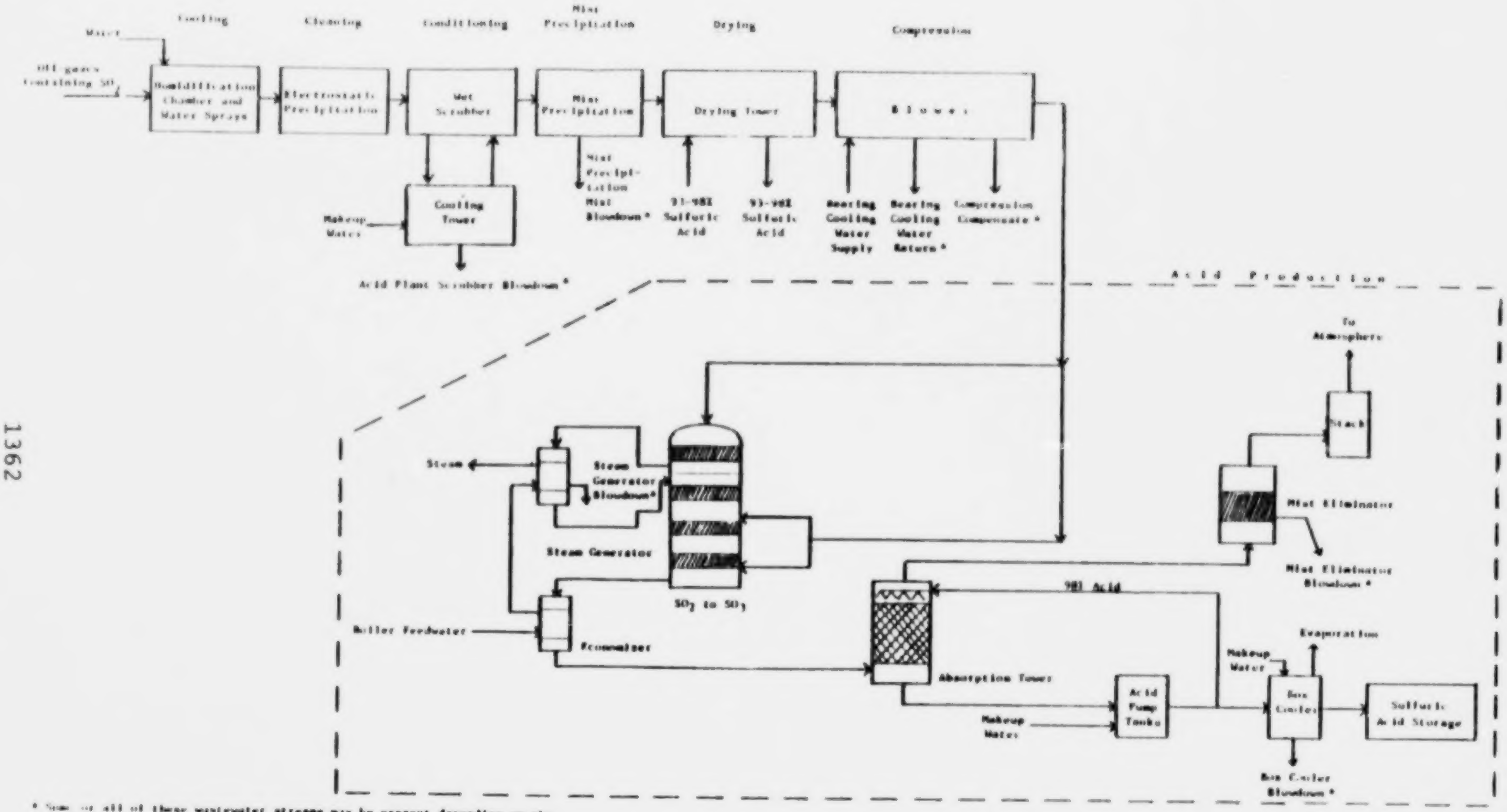
SUMMARY OF DISCHARGE STATUS IN THE METALLURGICAL ACID PLANTS SUBCATEGORY

Discharge Status	Associated Metal Plant Copper	Lead	Zinc	Total
Direct	2	2	4	8
Indirect	0	0	2	2
Zero	8	1	0	9
Total	10	3	6	19

TABLE III-2

PRODUCTION RANGE FOR METALLURGICAL ACID PLANTS

Production Range (kkg/yr 100% H_2SO_4)	Number of Plants
0 - 50000	2
50001 - 100000	4
100001 - 200000	5
200001 - 300000	5
300001 - Above	3


Off gases containing SO_2
Water
Cooling
Humidification Chamber and Water Sprays
Cleaning
Electrostatic Precipitation
Conditioning
Wet Scrubber
Cooling Tower
Makeup Water
Acid Plant Scrubber Blowdown *
Mist Precipitation
Mist Precipitation
Mist Precipitation Mist Blowdown *
Drying
Drying Tower
93-98% Sulfuric Acid
93-98% Sulfuric Acid
Compression
Blower
Bearing Cooling Water Supply
Bearing Cooling Water Return *
Compression Condensate *
Acid Production
Steam
Steam Generator Blowdown*
Steam Generator
Boiler Feedwater
Economizer
SO_2 to SO_3
Absorption Tower
98% Acid
Mist Eliminator
Mist Eliminator Blowdown *
Stack
To Atmosphere
Makeup Water
Acid Pump Tanks
Makeup Water
Evaporation
Box Cooler
Box Cooler Blowdown *
Sulfuric Acid Storage

* Some or all of these wastewater streams may be present depending on the specific plant configuration. These wastewaters are usually combined into a single acid plant blowdown stream which is treated and then recycled or discharged.

Figure III-1

TYPICAL METALLURGICAL ACID PLANT BLOCK FLOW DIAGRAM

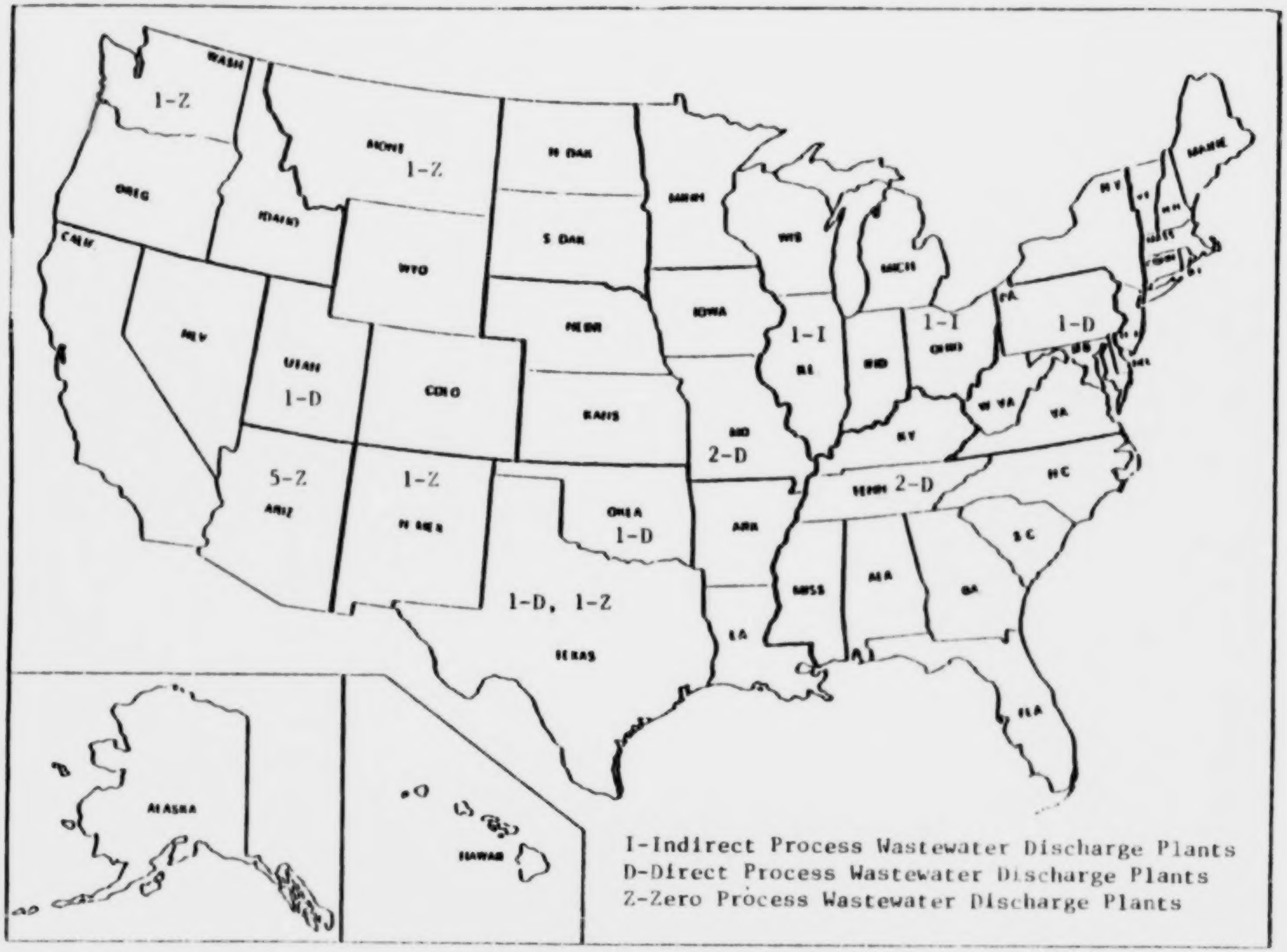

WASH
1-Z
MONT
1-Z
N DAK
OREG
IDAHO
S DAK
MINN
WIS
MICH
MAINE
NY
CALIF
WYO
NEBR
IOWA
1-I
ILL
IND
1-I
OHIO
PA
1-D
NEV
UTAH
1-D
COLO
KANS
MO
2-D
KY
W VA
VA
5-Z
ARIZ
1-Z
N MEX
OKLA
1-D
ARK
TENN 2-D
NC
SC
1-D, 1-Z
TEXAS
MISS
ALA
GA
LA
FLA
ALASKA
HAWAII
I-Indirect Process Wastewater Discharge Plants
D-Direct Process Wastewater Discharge Plants
Z-Zero Process Wastewater Discharge Plants

Figure III-2

GEOGRAPHIC LOCATIONS OF METALLURGICAL ACID PLANTS

SECTION IV

SUBCATEGORIZATION

This section summarizes the factors considered during the designation of the metallurgical acid plants subcategory and its related subdivisions.

The metallurgical acid plants subcategory was created in the rulemaking of July 2, 1980 (45 FR 44926) to limit the mass of toxic pollutants discharged from the production of sulfuric acid at copper smelters. Only BPT effluent limitations were established in that rulemaking. As discussed in Section 1, the initial metallurgical acid plants subcategory included all operations associated with the manufacture of sulfuric acid at primary copper plants and included associated air pollution control (or gas conditioning systems) for sulfur dioxide off-gases from pyrometallurgical operations. On March 8, 1984 (49 FR 8742), EPA expanded the metallurgical acid plants subcategory to include the production of sulfuric acid in primary lead and primary zinc plants and further expanded the coverage to include sulfuric acid production at primary molybdenum plants in a rulemaking on September 20, 1985. The 1984 and 1985 rulemakings promulgated BAT limitations and new source and pretreatment standards for this subcategory.

FACTORS CONSIDERED IN SUBDIVIDING THE METALLURGICAL ACID PLANT SUBCATEGORY

EPA examined the 14 factors listed previously to determine if the metallurgical acid plants subcategory should be subdivided. Subdivision within the nonferrous metals subcategories allows separate analysis of distinct wastewater streams. If significant and distinct wastewater streams which have clearly different origins can he identified within a subcategory, then segmentation is indicated. For the metallurgical acid plants subcategory, separation into segments was determined to be unnecessary. For this subcategory a single all encompassing building block, "acid plant blowdown," has been designated. The effluent limitations and standards for the metallurgical acid plants subcategory are based on analyses of flow and pollutant composition data for the acid plant blowdown stream.

As discussed in Section III, several wastewater streams are usually combined to form a single acid plant blowdown stream. While different acid plants may combine somewhat different streams to form the acid plant blowdown stream, most of the wastewater streams which combine to form the acid plant blowdown stream have similar characteristics with respect to two of the more important relevant subcategorization factors. These factors are as follows:

1. Raw materials--most of the wastewater streams which may

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be combined to form the acid plant blowdown stream are produced by removing condensates and particulate matter from gases containing SO_2; and

2. Manufacturing processes--the unit operations (scrubbing, mist precipitation, compression, etc.) involved in pretreating the gas and making acid are similar from one acid plant to another.

Depending on air quality requirements, acid plants may incorporate a double contact system with the converter to achieve lower SO_2 concentrations of the effluent gas. Although a double contact acid plant reduces the concentration of SO_2, it does not increase the volume of wastewater generated in an acid plant. A double contact acid plant recycles the effluent gas stream back to the converters after absorption for additional conversion of SO_2 to SO_3 There is no gas conditioning or cleaning required for gaseous emissions to be recycled. Therefore, the differences in manufacturing processes of single and double contact acid plants do not require separate subcategorization.

PRODUCTION NORMALIZING PARAMETERS

The effluent limitations and standards developed in this document establish mass limits on the discharge of specific pollutant parameters. To allow these to be applied to plants with various production levels, the mass of pollutant discharged must be related to a unit of production. This factor is known as the production normalizing parameter (PNP). Acid plant production is reported as a percentage of acid contained within the final product. For example, a plant may report its yearly acid production as 100 tons of 85 percent sulfuric acid. So that the wastewater generated within each acid plant can be compared, it must be related to a common basis such as 100 percent sulfuric acid production. Data from the 1977 data collection portfolios indicate that acid plant water use and blowdown correlated better with acid plant capacity than with actual acid plant production. Thus, the production normalizing parameter is the production capacity of sulfuric acid on a 100 percent acid basis.

SECTION V

WATER USE AND WASTEWATER CHARACTERISTICS

This section describes the characteristics of wastewater associated with the metallurgical acid plants subcategory. Data used to quantify wastewater flow and pollutant concentrations are presented, summarized, and discussed. The contribution of specific production processes to the overall wastewater discharge from metallurgical acid plants is identified whenever possible.

The two principal data sources used in the development of these limitations and standards were the data collection portfolios and field sampling results. Data collection portfolios contain information regarding wastewater flows and production levels. Data gathered through comments on the proposed mass limitations and Section 308 requests are also principal data sources.

In order to quantify the pollutant discharge from metallurgical acid plants, a field sampling program was conducted. Wastewater samples were collected in two phases: screening and verification. The first phase, screen sampling, was to identify which toxic pollutants were present in wastewaters from production of the various metals. Screening samples were analyzed for 128 of the 126 priority pollutants and other pollutants deemed appropriate. (Because the analytical standard for TCDD was judged to be too hazardous to be made generally available, samples were never analyzed for this pollutant. There is no reason to expect that TCDD would be present in metallurgical acid plant wastewaters). A total of 10 plants were selected for screen sampling in the nonferrous metals manufacturing category. A complete list of the pollutants considered and a summary of the techniques used in sampling and laboratory analyses are included in Section V of Vol. 1. In general, the samples were analyzed for three classes of pollutants: priority organic pollutants, priority metal pollutants, and criteria pollutants (which includes both conventional and nonconventional pollutants). A verification sampling effort was conducted at one primary zinc plant between proposal and promulgation. Acid plant blowdown was one of the waste streams sampled. The Agency believed additional process and wastewater data were needed to better characterize the primary zinc subcategory. Also, sampling was conducted at one metallurgical acid plant associated with primary molybdenum roasting operations as a part of nonferrous metals manufacturing.

As described in Section IV of this supplement, the wastewaters from metallurgical acid plants in primary copper, primary lead, primary molybdenum, and primary zinc plants (and wastewaters from SO_2 off-gas conditioning or control operations) are all included in the single wastewater stream termed "acid plant blowdown" in this document.

WATER USE AND WASTEWATER DISCHARGE RATES

Two flow-to-production ratios for each acid plant were calculated using information supplied in the data collection portfolios. The two ratios, water use and wastewater discharge flow, are differentiated by the flow value used in calculation. Water use is defined as the volume of water required per ton of sulfuric acid capacity (on a 100 percent acid basis) and is therefore based on the sum of recycle and makeup flows. Wastewater flow discharged after pretreatment or recycle (if these are present) is used in calculating the production normalized flow--the volume of wastewater discharged from a given process to further treatment, disposal, or discharge per ton of 100 percent acid capacity. Differences between the water use and wastewater discharge flow rates result from recycle or evaporation. The production capacity values used in the calculation correspond to the production normalizing parameter, PNP, as discussed in Section IV.

The two water-to-production ratios for each acid plant are shown in Table V-1 (page 1371). This table also gives the percent recycle, which is calculated from these two ratios.

Since the data collection portfolios have been collected, the Agency has learned that two primary zinc plants, one primary lead plant, and one primary copper plant have closed or no longer produce these metals. Flow and production data (when available) for these plants are presented in this section and in the remainder of this document. Although these plants are currently not operating, these data are an integral part of the BAT effluent limitations because as representative processes their information remains relevant in determining what constitutes best available technology. Therefore, it is necessary to present this information so that the BAT limitations are documented.

WASTEWATER CHARACTERISTICS

In order to quantify the concentrations of pollutants present in the blowdown stream from acid plants, wastewater samples were collected at eight plants. Diagrams indicating the sampling points are shown in Figures V-1 through V-8 (pages 1381 - 1388). These diagrams also indicate some of the ways in which different wastewater sources are combined to produce the acid plant blowdown stream.

The acid plant blowdown stream sampling data is presented in Table V-2 (page 1372). Where no data is listed for a specific day of sampling, the wastewater samples for the stream were not collected. If the analysis did not detect a pollutant in a waste stream, the pollutant was omitted from the table. The method by which each sample was collected is indicated by number, as follows:

1	one-time grab
2	24-hour manual composite

3	24-hour automatic composite
4	48-hour manual composite
5	48-hour automatic composite
6	72-hour manual composite
7	72-hour automatic composite

The data tables include some samples measured at concentrations considered not quantifiable. The base-neutral extractable, acid extractable, and volatile organics are generally considered not quantifiable at concentrations equal to or less than 0.010 mg/l. Below this concentration, organic analytical results are not quantitatively accurate; however, the analyses are useful to indicate the presence of a particular pollutant. The pesticide fraction is considered nonquantifiable at concentrations equal to or less than 0.005 mg/l. Nonquantifiable results are designated in the tables with an asterisk (double asterisk for pesticides).

The detection limits shown on the data tables are not the same as published detection limits for these pollutants by the same analytical methods. The detection limits used were reported with the analytical data and hence are the appropriate limits to apply to the data. Detection limit variation can occur as a result of a number of laboratory-specific, equipment-specific, and daily operator-specific factors. These factors can include day-to-day differences in machine calibration, variation in stock solutions, and variation in operators.

The statistical analysis of data includes some samples measured at concentrations considered not quantifiable. Data reported as an asterisk are considered as detected but below quantifiable concentrations, and a value of zero is used for averaging. Priority organic, nonconventional, and conventional data reported with a "less than" sign are considered as detected, but not further quantifiable. A value of zero is also used for averaging. If a pollutant is reported as not detected, it is excluded in calculating the average. Finally, priority metal values reported as less than a certain value were considered as not detected and a value of zero is used in the calculation of the average. For example, three samples reported as ND, *, and 0.021 mg/l have an average value of 0.010 mg/l. The averages calculated are presented with the sampling data; these values were not used in the selection of pollutant parameters.

As discussed in Section III, the acid plant blowdown stream is normally a combination of several streams related to the manufacture of sulfuric acid from SO_2 off-gases from metallurgical operations. Typical potential components of this stream include:

1. Acid plant scrubber blowdown,
2. Mist precipitator blowdown,
3. Compression condensate,
4. Box cooler blowdown, and
5. Mist eliminator blowdown.

The acid plant blowdown stream sampling data given in Table V-2 are used in Section VI to determine which pollutants should be considered for regulation. The sampling data in Table V-2 indicate that the acid plant blowdown stream contains treatable concentrations of several metals (such as antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc), and suspended solids. The pH data indicate either acidic or basic wastewaters depending on the stream sampled. Priority organics were found at measurable concentrations in some streams.

TABLE V-1

WATER USE AND WASTEWATER DISCHARGE FLOW RATES FOR METALLURGICAL ACID PLANTS

(l/kkg (gal/ton) of 100% H_2SO_4 Capacity)

Wastewater				
Water	Use	Discharge	Percent	
Plant	Code	l/kkg (gal/ton)	l/kkg (gal/ton)	Recycle
206	Cu	459 (110)	0	100
285	Cu	NR	331.9(80)	NR
284	Pb	INC	745.5(179)	INC
7001	Cu	NR	748.9(180)	NR
4503	Cu	60690 (14550)	1214 (291)	98
283	Zn	62190 (14910)	1306 (313)	98
278	Zn	140000 (33560)	1351 (324)	99
213	Cu	175500 (42080)	1386 (332)	99
211	Cu	1468 (352)	1468 (352)	0
216	CU	82280 (19730)	1481 (355)	98
279	Zn	NR	2145 (514)	NR
212	Cu	4487 (1076)	2394 (563)	47
281	Zn	NR	4196 (1006)	NR
214	Cu	35800 (8580)	4904 (1176)	86
282	Zn!	6540 (1570)	5470 (1310)	0*
60	Cu	NR	6213 (1490)	NR
290	Pb	195500 (46870)	6238 (1496)	97
280	Pb!	19052 (4570)	6249 (1498)	67
280	Zn!	8609 (2064)	6457 (1548)	25
4201	Cu	NR	15840 (3798)	NR
288	Cu	INC	3362 (806)	INC
9060	Zn	NR	505 (121)	NR
6310	Zn	NR	NR	NR

NOTES: NR = Data not reported in dcp.
INC = Inconclusive data reported in dcp.
* = 100% Evaporation
! = Plant closed or no longer operating acid plant.

Table V-2

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Concentrations (mg/l, except as noted) Source	Day 1	Day 2	Day 3	Average
Toxic Pollutants							
1. acenaphthene	321	2		*	ND	ND	*
4. benzene	7	2		0.012	<0.015	<0.018	0.004
6. carbon tetrachloride	7	2		ND	ND	0.02	0.02
	88	3	ND	ND	0.041	*	0.02
	89	2	ND	ND	0.054	ND	0.054
	209	5		ND			
	212	2		ND			
10. 1,2-dichloroethane	7	2		0.044	0.06	ND	0.052
11. 1,1,1-trichloroethane	321	1	*	*	*	*	*
13. 1,1-dichloroethane	88	3	ND	ND	ND	ND	
	89	2	ND	ND	ND	ND	
	209	5		ND			
	212	2		0.18			0.18
15. 1,1,2,2-tetrachloroethane	88	3	*	<0.012	ND	ND	<0.012
	89	2	*	<0.012	ND	ND	<0.012
	209	5		ND			
	212	2		ND			
22. p-chloro-m-cresol	321	2	0.040	*	0.045	0.042	0.029
23. chloroform	7	2		0.396	0.082	0.054	0.177
	88	3	ND	*	*	0.023	0.008
	89	2	ND	ND	0.036	*	0.018
	209	5		ND			
	212	2		*			*
	321	1	0.013	*	*	ND	*

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Concentrations (mg/l, except as noted)				
			Source	Day 1	Day 2	Day 3	Average
29. 1,1-dichloroethylene	7	2		0.028	ND	0.113	0.071
	321	1		ND	ND	*	*
34. 2,4-dimethylphenol	321	2		*	*	ND	*
38. ethylbenzene	7	2		*	0.015	*	0.005
	321	2	0.049	ND	0.049	ND	0.049
44. methylene chloride	7	2		0.191	ND	ND	0.191
	88	3	ND	ND	ND	ND	
	89	2	ND	ND	ND	ND	
	209	5		0.224			0.224
	212	2		0.23			0.23
	321	1	0.013	*	0.016	*	0.005
47. bromoform (tribromomethane)	321	1	*	ND	*	*	*
48. dichlorobromomethane	88	3	ND	0.014	ND	ND	0.014
	89	2	ND	ND	ND	ND	
	209	5		ND			
	212	2		ND			
51. chlorodibromomethane	7	2		ND	ND	0.014	0.014
	88	3	ND	<0.013	ND	ND	<0.013
	89	2	ND	ND	ND	ND	
	209	5		ND			
	212	2		ND			
56. nitrobenzene	321	2		*	ND	ND	*
57. 2-nitrophenol	321	2	*	ND	ND	ND	
62. N-nitrosodiphenylamine	321	2		*	*	ND	*
64. pentachlorophenol	321	2		*	ND	ND	*
	212	2		*			*
65. phenol	321	2		*	*	ND	*
	212	2		*			*
66. bis(2-ethylhexyl) phthalate	7	3		*	0.017	0.021	0.013
	88	3	0.036	0.02	0.193	*	0.071
	89	2	0.036	*	*	0.044	0.015
	209	5		0.022			0.022
	212	2		0.095			0.095
	321	2	0.040	ND	*	0.027	0.013

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Source	Concentrations (mg/l, except as noted) Day 1	Day 2	Day 3	Average
68. di-n-butyl phthalate	7	3		0.013	*	ND	0.0065
	321	2	*	*	*	*	*
78/81. anthracene/phenanthrene (e)	88	3	ND	ND	0.021	<0.012	0.01
	89	2	ND	ND	<0.017	*	<0.014
	209	5		ND			
	212	2		ND			
	321	2		*	ND	ND	*
85. tetrachloroethylene	7	2		0.023	*	*	0.008
	88	3	*	<0.013	0.011	ND	0.0055
	89	2	*	<0.015	*	*	0.005
	209	5		ND			
	212	2		ND			
86. toluene	321	1	ND	ND	ND	*	*
	88	3	ND	*	ND	ND	*
	89	2	ND	ND	ND	ND	
	209	5		0.057			0.057
	212	2		ND			
87. trichloroethylene	7	2		0.066	<0.082	<0.084	0.022
	321	1	*	ND	*	*	*
99. endrin aldehyde	321	2		*	*	ND	*
102. alpha-BHC	321	2	ND	ND	*	ND	*
103. beta-BHC	321	2	*	ND	*	*	*
105. delta-BHC	321	2		ND	ND	*	*
114. antimony	7	3		0.1	<0.002	0.05	0.075
	88	3	<0.1	3.4	3.6	<0.1	2.3
	89	2	<0.1	51	30	<0.1	27
	201	1	<0.01	<0.01			<0.01
	209	5		<1.5			<1.5
	212	2		0.05			0.05
	223	2		<0.100			<0.100
	321	2	<0.01	<0.01	<0.01	<0.01	<0.01

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Source	Day 1	Day 2	Day 3	Average
			Concentrations (mg/l, except as noted)				
115. arsenic	7	3		1.5	9.5	3.5	4.833
	88	3	0.01	200	350	36	195.3
	89	2	0.01	4,300	4,700	80	3,027
	201	1	<0.005	0.018			0.018
	209	5		<2.622			<2.622
	212	2		0.28			0.28
	223	2		40.0			40.0
	321	2	<0.01	<0.01	<0.01	<0.01	<0.01
116. asbestos	7	1	ND		1,200(MFL)		1,200
117. beryllium	7	3		0.012	0.008	0.006	0.0087
	88	3	<0.001	<0.01	0.01	0.002	0.004
	89	2	<0.001	<0.001	<0.001	<0.001	<0.001
	209	5		<0.02			<0.02
	212	2		<0.02			<0.02
	223	2		<0.005			<0.005
	321	2	<0.005	<0.005	<0.005	<0.005	<0.005
118. cadmium	7	3		5	5	5	5
	88	3	<0.002	10	20	<1	10
	89	2	<0.002	0.7	0.9	3	1.53
	201	1	<0.001	0.044			0.044
	209	5		42.13			42.13
	212	2		1.93			1.93
	223	2		<0.005			<0.005
	321	2	<0.02	2.96	1.56	1.46	1.99
119. chromium	7	3		0.907	0.697	0.539	0.714
	88	3	<0.005	<0.05	0.10	0.09	0.063
	89	2	<0.005	0.02	0.02	0.05	0.03
	201	1	<0.005	0.011			0.011
	209	5		0.112			0.112
	212	2		0.06			0.06
	223	2		0.08			0.08
	321	2	<0.02	<0.02	<0.02	<0.02	<0.02

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Source	Concentrations (mg/l, except as noted) Day 1	Day 2	Day 3	Average
120. copper	7	3		0.692	0.603	0.503	0.600
	88	3	0.02	500	600	300	467
	89	2	0.02	100	80	70	83.3
	201	1	0.026	0.082			0.082
	209	5		24.53			24.53
	212	2		1.88			1.88
	223	2		11.0			11.0
	321	2	<0.05	1.35	1.8	1.5	1.55
121. cyanide	7	3		0.003	0.003	0.004	0.0033
	223	2		<0.02			<0.02
	321	1	<0.02	<0.02	<0.02	<0.02	<0.02
122. lead	7	3		3	3	3	3
	88	3	0.02	100	400	0.4	167
	89	2	0.02	1	1	8	3.33
	201	1	0.014	1.6			1.6
	209	5		16.65			16.65
	212	2		5.68			5.68
	223	2		1.20			1.20
	321	2	<0.05	5.55	3.95	4.0	4.5
123. mercury	88	3	0.0001	0.064	0.06	0.007	0.044
	89	2	0.0001	0.18	0.09	0.0006	0.0902
	201	1	<0.0002	<0.0002			<0.0002
	209	5		<0.004			<0.004
	212	2		0.0516			0.0516
	223	2		0.006			0.006
	321	2	<0.001	2.80	<0.001	1.60	1.46
124. nickel	7	3		6	4	3	4.33
	88	3	<0.005	0.6	0.6	0.9	0.7
	89	2	<0.005	0.1	0.06	0.2	0.12
	201	1	<0.02	0.04			0.04
	209	5		<0.009			<0.009
	212	2		0.175			0.175
	223	2		0.700			0.700
	321	2	<0.05	0.05	<0.05	<0.05	0.016

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Source	Concentrations (mg/l, except as noted) Day 1	Day 2	Day 3	Average
125. selenium	7	3		<0.002	0.2	0.1	0.10
	88	3	<0.01	0.01	0.01	<0.01	0.006
	89	2	<0.01	0.14	0.18	<0.01	0.11
	201	1	<0.005	<0.005			<0.005
	209	5		0.352			0.352
	212	2		0.445			0.445
	223	2		1.20			1.20
	321	2	<0.05 (g)	1.3	0.29	(f)	0.79
126. silver	88	3	<0.02	0.59	0.38	0.12	0.36
	89	2	<0.02	4.9	1.2	0.03	2.04
	201	1	<0.001	<0.001			<0.001
	209	5		0.0126			0.0126
	212	2		0.09			0.09
	223	2		0.230			0.230
	321	2	<0.01	0.01	0.01	0.01	0.01
127. thallium	88	3	<0.1	<0.1	<0.1	<0.1	<0.1
	89	2	<0.1	1.2	0.6	<0.1	0.6
	201	1	<0.005	<0.005			<0.005
	209	5		0.319			0.319
	212	2		<0.02			<0.02
	223	2		<0.100			<0.100
	321	2	<0.01	<0.01	<0.01	<0.01	<0.01
128. zinc	7	3		100	100	100	100
	88	3	<0.06	200	200	60	153
	89	2	<0.06	20	20	50	30
	201	1	0.047	1.19			1.19
	209	5		77.7			77.7
	212	2		224			224
	223	2		0.230			0.230
	321	2	0.06	512.01	259.0	243.0	338.0
Nonconventionals							
acidity	321	2	<1	1,200	16,800	16,000	11,333
alkalinity	321	2	73	<1	<1	<1	<1

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Concentrations (mg/l, except as noted) Source	Day 1	Day 2	Day 3	Average
aluminum	321	2					
ammonia	201	1	0.4	0.4			0.4
	321	2	<1	<1	<1	<1	<1
barium	321	2	<0.05	0.15	0.05	0.05	0.08
boron	321	2	<0.10	0.4	0.4	0.6	0.46
calcium	321	2	37.2	46.3	40.5	38.5	41.7
chemical oxygen demand (COD)	7	3		76	56	46	59.3
	88	3	<5	268	367	686	440.3
	89	2	<5	12,890	10,810	28	7,190
	201	1	30	11			11
	223	2		104			104
	321	2	<1	227	146	227	200
chloride	321	2	5	2,330	1,550	1,375	1,751
cobalt	321	2	<0.05	<0.05	<0.05	<0.05	<0.05
fluoride	321	2	0.1	<0.1	77	87	54
iron	321	2	0.30	3.35	2.1	4.75	3.4
magnesium	321	2	5.50	8.1	6.8	6.3	7.0
manganese	321	2	<0.05	0.05	0.05	0.10	0.06
molybdenum	321	2	<0.05	<0.05	<0.05	<0.05	<0.05
phenols (total; by 4-AAP method)	7	2		0.002	0.01	0.001	0.004
	88	3		0.002	<0.001	0.011	0.004
	89	2		0.039	0.014	0.007	0.020
	201	1	0.008	0.016			0.016
	223	2		<0.002			<0.002
	321	1	<0.005	<0.005	<0.005	<0.005	<0.005

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

			Concentrations (mg/l, except as noted)				
Pollutant (a,b,c,d,e,f,g,h)	Stream Code	Sample Type †	Source	Day 1	Day 2	Day 3	Average
phosphate	321	2	0.26	0.08	0.30	0.32	0.23
sodium	321	2	4.10	5.0	4.6	4.6	4.7
sulfate	321	2	36	8,680	11,300	11,800	10,593
tin	321	2	0.50	<0.5	<0.5	<0.5	0.35
titanium	321	2	<0.05	0.1	<0.05	0.05	0.11
total dissolved solids (TDS)	321	2	189	9,770	<16,400(h)	<16,400(h)	3,256
total organic carbon (TOC)	7	3		10	9	9	9.33
	88	3	3	3	8	8	6.33
	89	2	3	13	19	1	11
	223	2		8			8
	321	2	3	5	4	4	4.3
total solids (TS)	321	2	200	<12,800(h)	<17,000(h)	15,800(h)	15,200
vanadium	321	2	<0.05	<0.05	<0.05	<0.05	<0.05
yttrium	321	2	<0.05	<0.05	<0.05	<0.05	<0.05
Conventionals							
oil and grease	7	1		13	13	16	14
	88	1		8	9	163	60
	89	1		7	12	2	7
	321	1	3	13	1	<1	4.6
total suspended solids (TSS)	7	3		23	12	9	14.8
	88	3	1	6,090	4,720	1,622	4,145
	89	2	1	12,450	23,740	210	12,310
	201	1	45	10			10
	223	2		10			10
	321	2	1	10	25	30	21

Table V-2 (Continued)

METALLURGICAL ACID PLANTS SAMPLING DATA
ACID PLANT BLOWDOWN

Pollutant (a,b,c,d,e,f,g)	Stream Code	Sample Type †	Source	Concentrations (mg/l, except as noted) Day 1	Day 2	Day 3	Average
pH (standard units)	7	1		2	2.3	2.1	
	88	1			11.4	11.5	
	89	1		2.6		4.5	
	201	1	7.3	8.4			
	223	2		2.10			
	321	2	6	1.0	0.6	1.0	

(a) One sample from stream 209 was analyzed for acid extractable toxic organic pollutants; none was detected. Seven samples from three streams were analyzed for the pesticide fraction; none of these pollutants was detected above its analytical quantification concentration.

(b) One sample for stream code 201 was analyzed for the toxic organic pollutants, cyanide, and asbestos. None was reported present above its analytical quantification concentration.

(c) Three samples for stream 7 were analyzed for the acid extractable toxic pollutants, and three samples for the pesticide fraction; none of these pollutants was reported above its analytical quantification concentration.

(d) Three samples from stream 321 were analyzed for all toxic organic fractions.

(e) Reported together, except for stream 321 - values are for phenanthrene only.

(f) Interference.

(g) Detection limit raised due to interference.

(h) Sulfuric acid interference.

† Sample Type.

1	one-time grab
2	24-hour manual composite
3	24-hour automatic composite
4	48-hour manual composite
5	48-hour automatic composite
6	72-hour manual composite
7	72-hour automatic composite

*Less than or equal to 0.01 mg/l.

**Less than or equal to 0.005 mg/l.

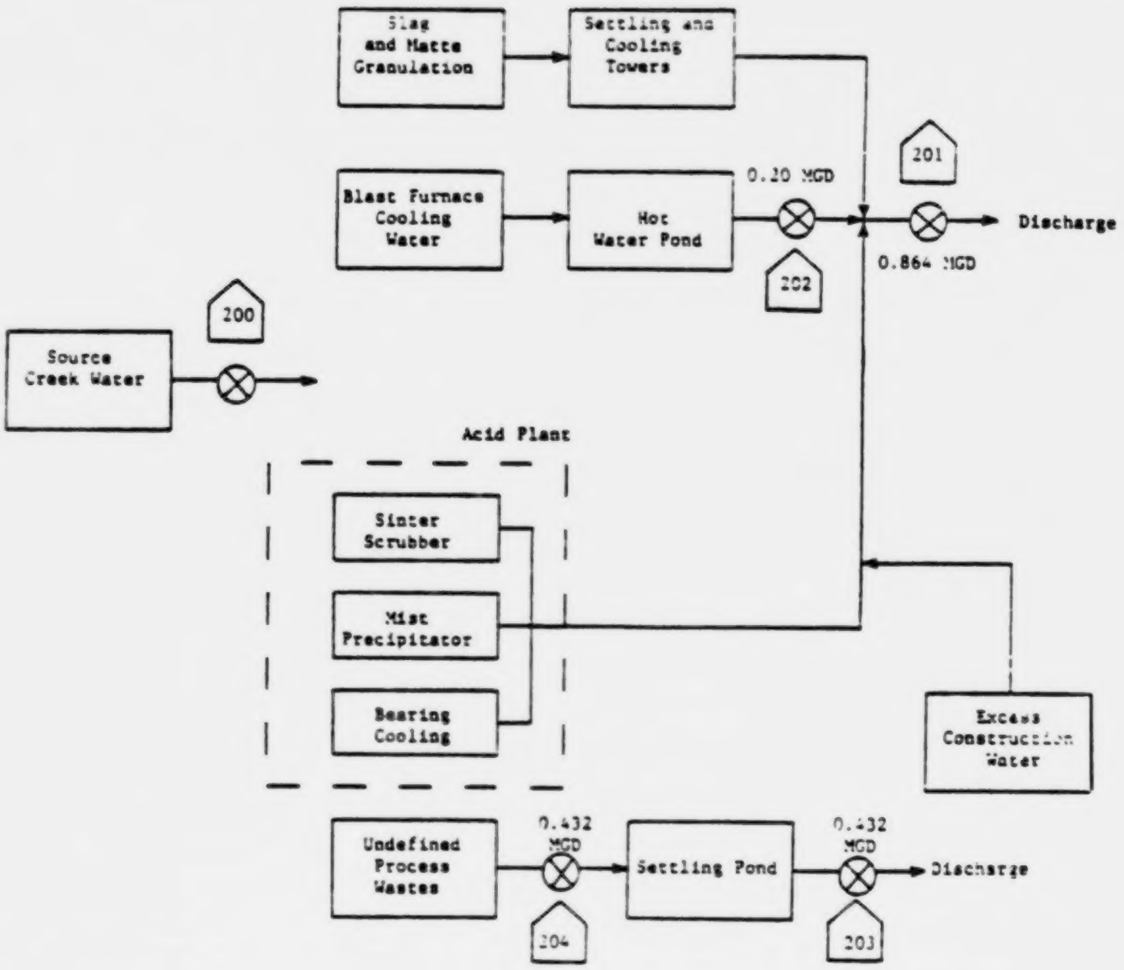
Slag and Matte Granulation
Settling and Cooling Towers
201
Blast Furnace Cooling Water
Hot Water Pond
0.20 MGD
202
Discharge
0.864 MGD
200
Source Creek Water
Acid Plant
Sinter Scrubber
Mist Precipitator
Bearing Cooling
Excess Construction Water
Undefined Process Wastes
0.432 MGD
204
Settling Pond
0.432 MGD
203
Discharge

FIGURE V-1

SAMPLING SITES AT PRIMARY LEAD PLANT B

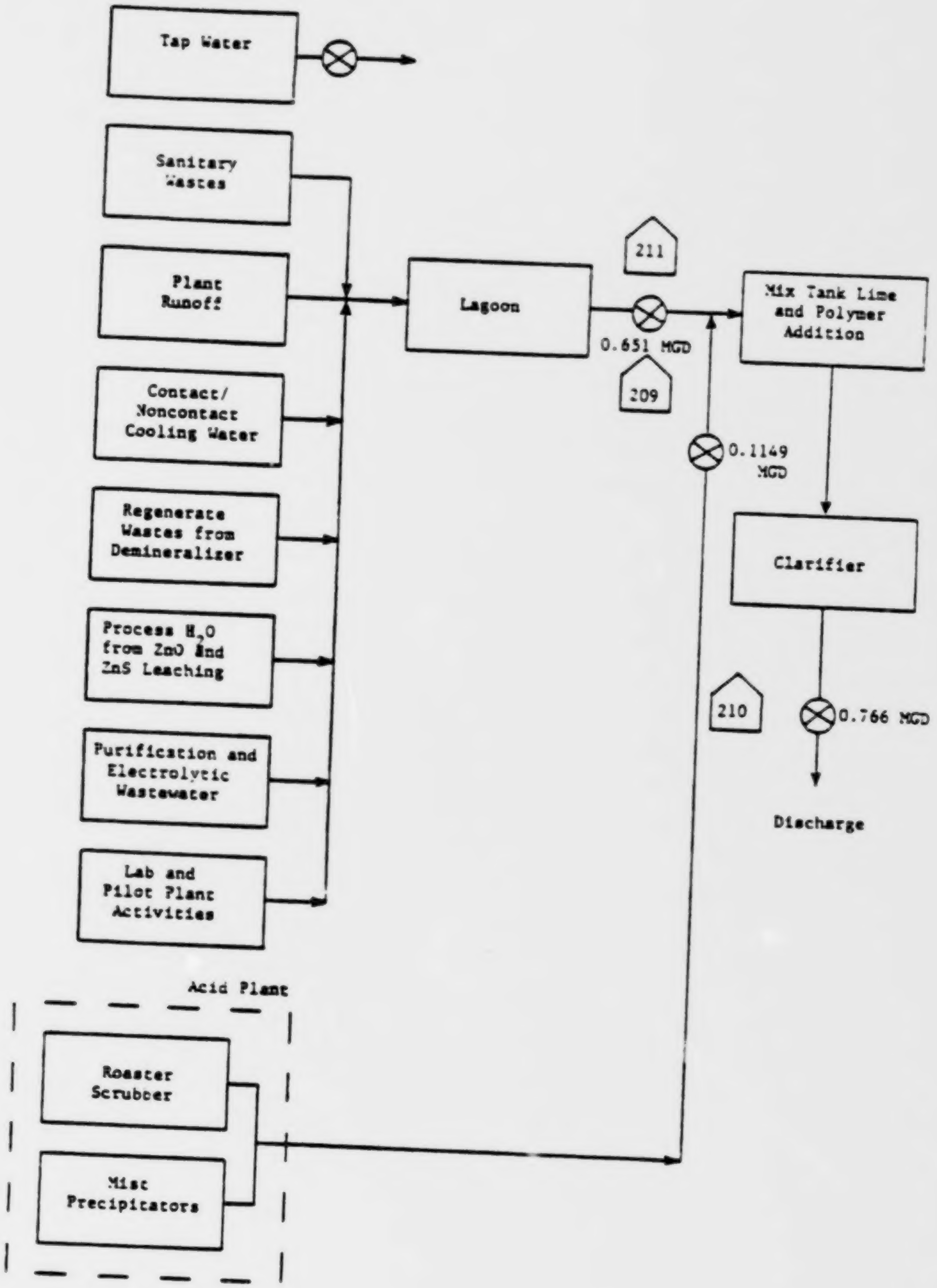
Tap Water
Sanitary Wastes
Plant Runoff
Contact/ Noncontact Cooling Water
Regenerate Wastes from Demineralizer
Process H_2O from ZnO and ZnS Leaching
Purification and Electrolytic Wastewater
Lab and Pilot Plant Activities
Acid Plant
Roaster Scrubber
Mist Precipitators
Lagoon
211
0.651 MGD
209
0.1149 MGD
Mix Tank Lime and Polymer Addition
Clarifier
210
0.766 MGD
Discharge

FIGURE V-2

SAMPLING SITES AT PRIMARY ZINC PLANT B

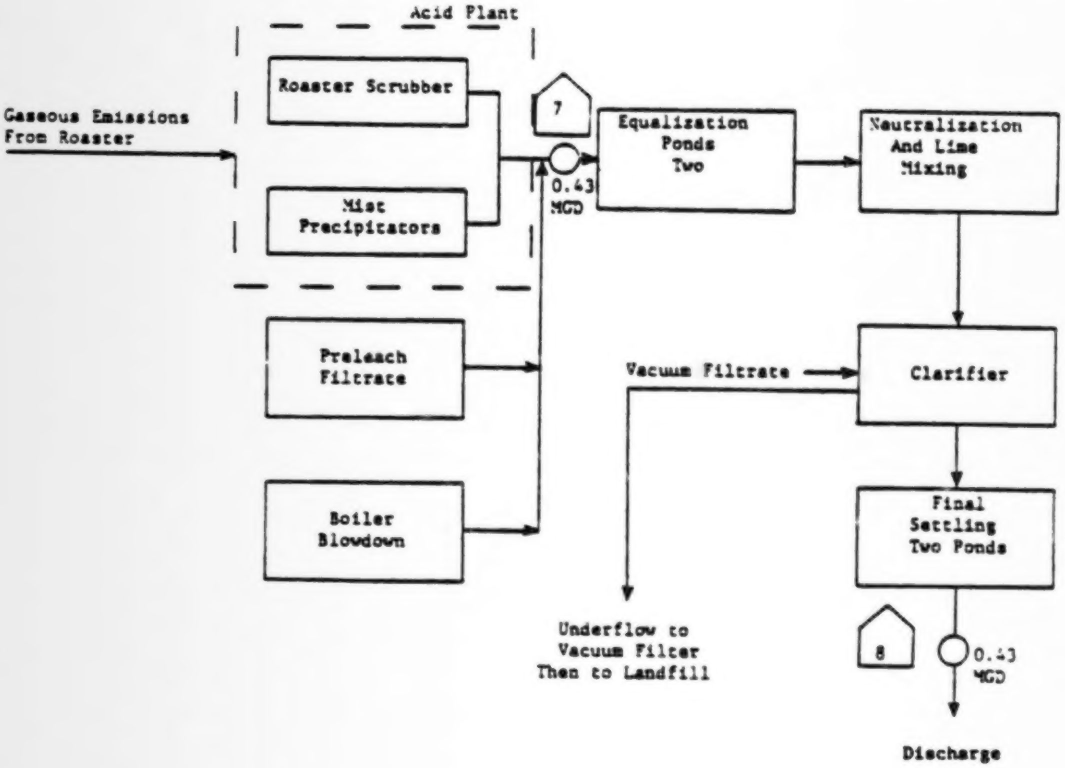
Acid Plant
Gaseous Emissions From Roaster
Roaster Scrubber
Mist Precipitators
7
0.43 MGD
Equalization Ponds Two
Neutralization And Lime Mixing
Preleach Filtrate
Boiler Blowdown
Vacuum Filtrate
Clarifier
Final Settling Two Ponds
Underflow to Vacuum Filter Then to Landfill
8
0.43 MGD
Discharge

FIGURE V-3

SAMPLING SITES AT PRIMARY LEAD PLANT C

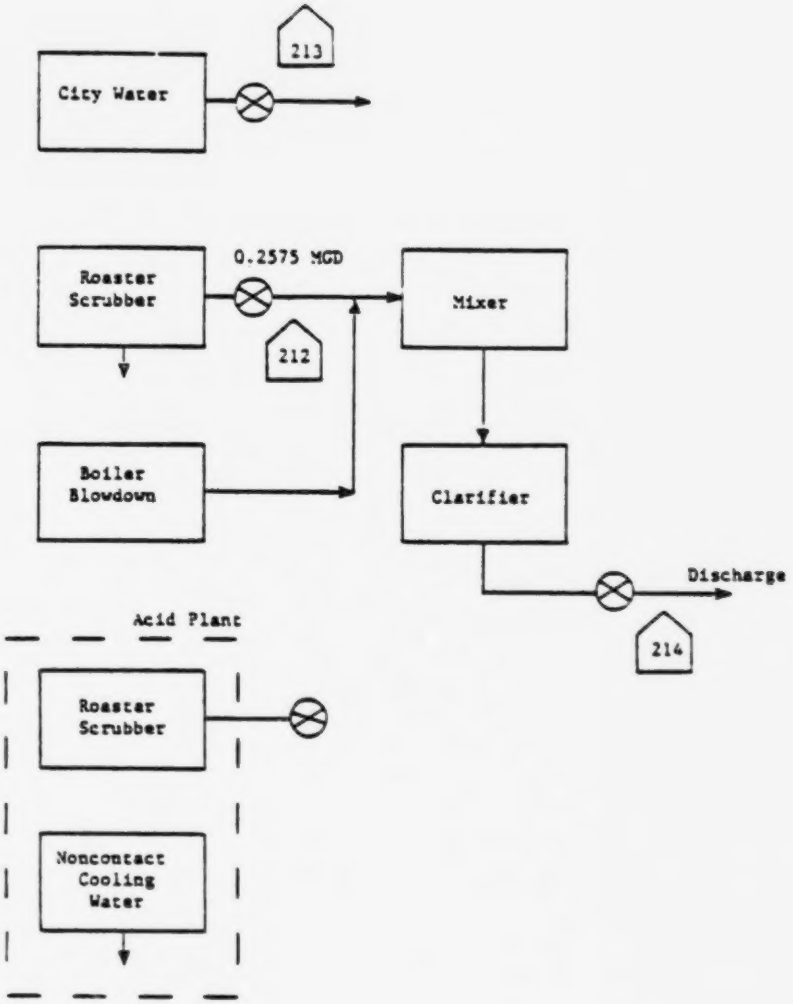
213
City Water
0.2575 MGD
Roaster Scrubber
212
Mixer
Boiler Blowdown
Clarifier
Discharge
214
Acid Plant
Roaster Scrubber
Noncontact Cooling Water

FIGURE V-4

SAMPLING SITES AT PRIMARY ZINC PLANT D

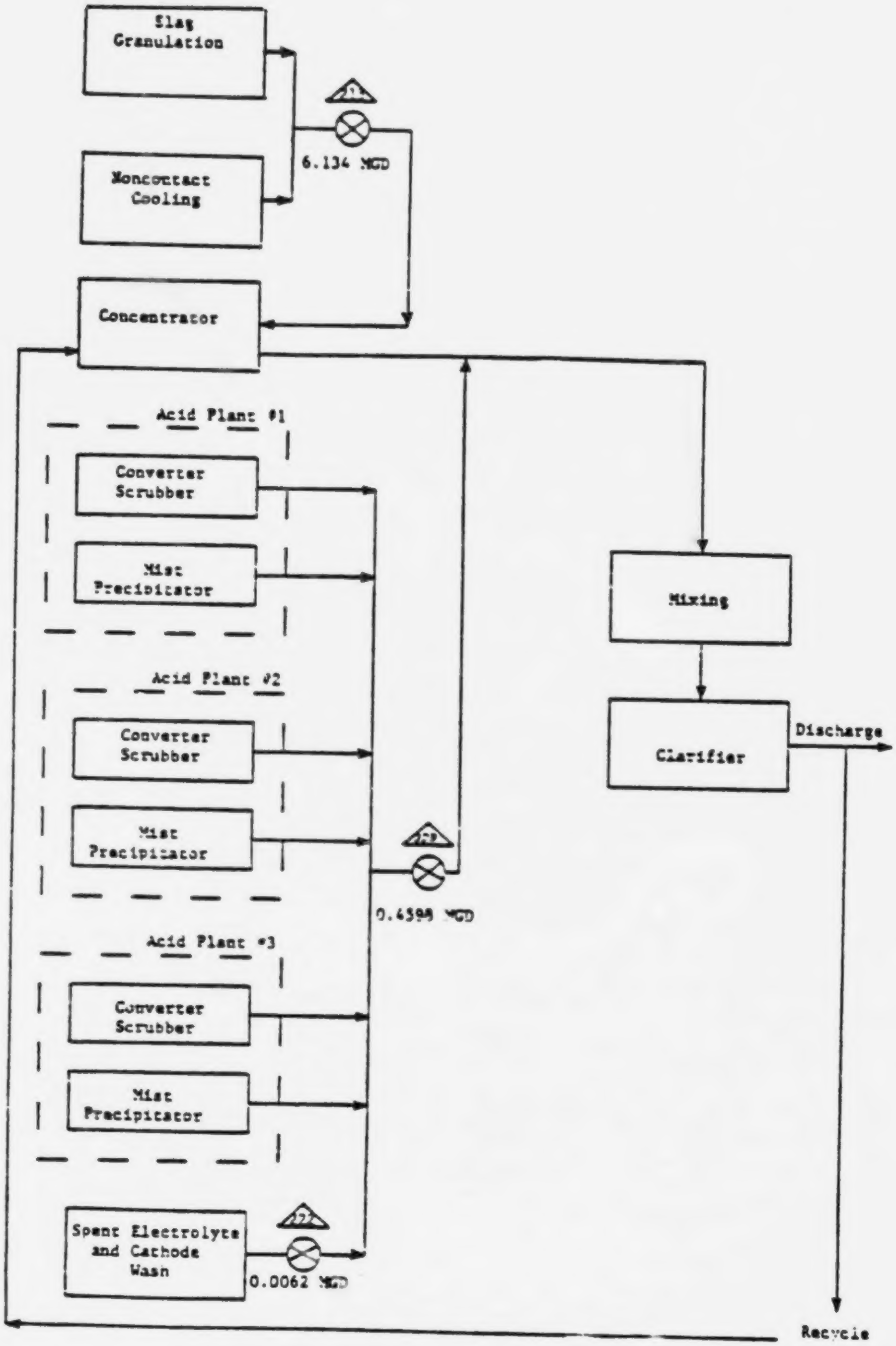
Slag Granulation
Noncontact Cooling
6.134 MGD
Concentrator
Acid Plant #1
Converter Scrubber
Mist Precipitator
Acid Plant #2
Converter Scrubber
Mist Precipitator
0.4598 MGD
Acid Plant #3
Converter Scrubber
Mist Precipitator
Spent Electrolyte and Cathode Wash
0.0062 MGD
Mixing
Clarifier
Discharge
Recycle

FIGURE V-5

SAMPLING SITES AT PRIMARY COPPER SMELTING AND REFINING PLANT C

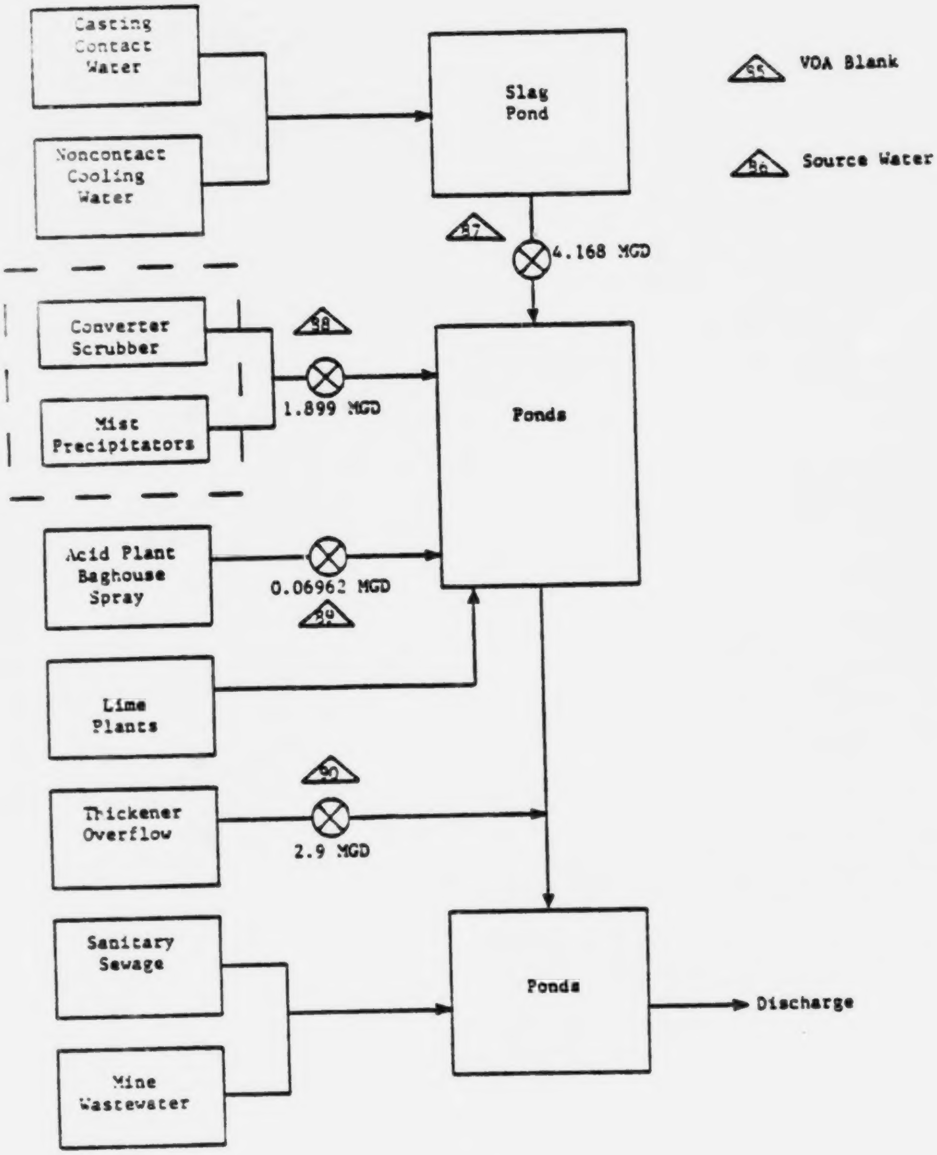
Casting Contact Water
Noncontact Cooling Water
Slag Pond
95
VOA Blank
86
Source Water
87
4.168 MGD
Converter Scrubber
Mist Precipitators
88
1.899 MGD
Ponds
Acid Plant Baghouse Spray
0.06962 MGD
89
Lime Plants
90
Thickener Overflow
2.9 MGD
Sanitary Sewage
Mine Wastewater
Ponds
Discharge

FIGURE V-6

SAMPLING SITES AT PRIMARY COPPER SMELTER PLANT B

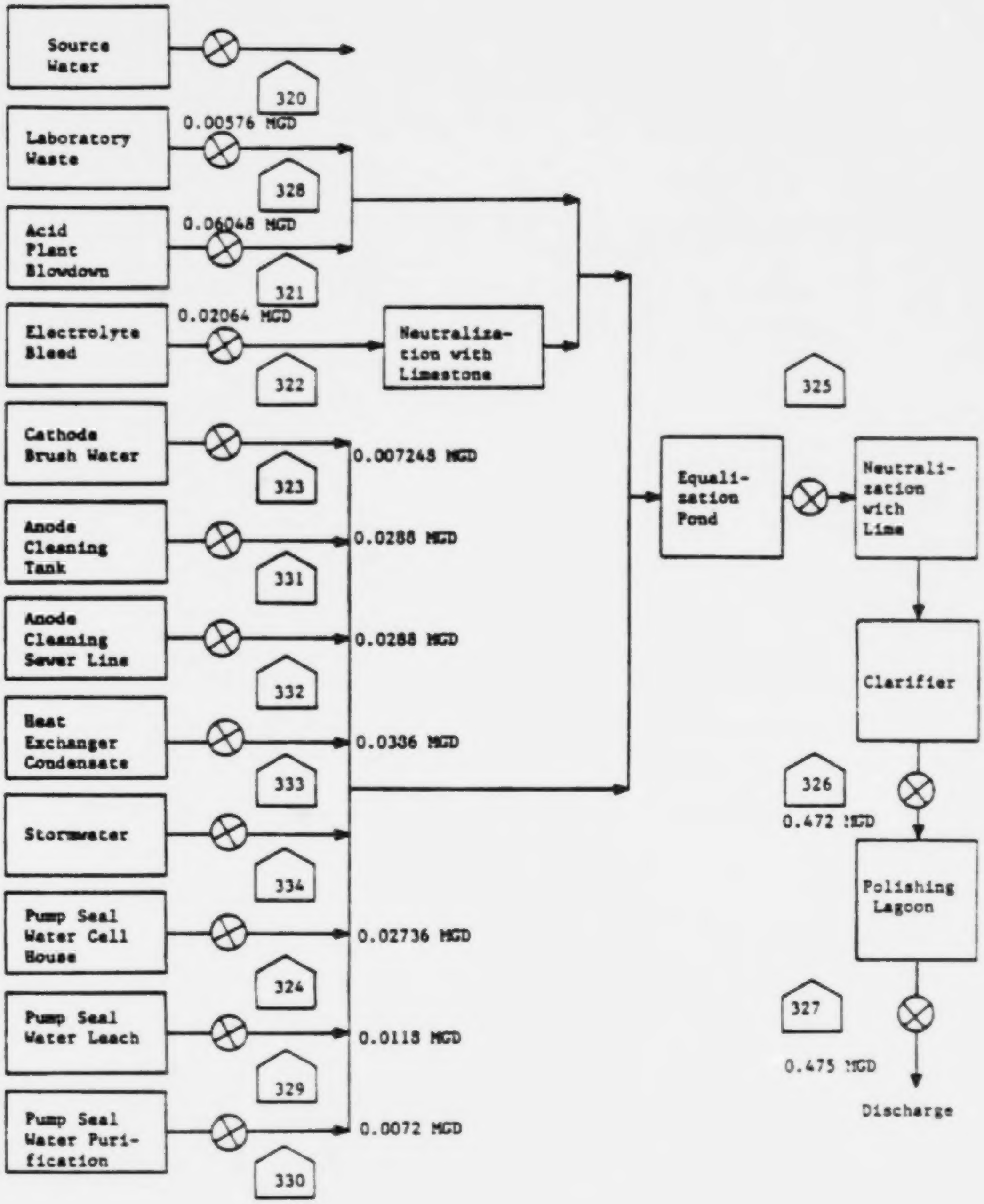
Source Water
320
Laboratory Waste
0.00576 MGD
328
Acid Plant Blowdown
0.06048 MGD
321
Electrolyte Bleed
0.02064 MGD
322
Neutralization with Limestone
Cathode Brush Water
0.007248 MGD
323
Anode Cleaning Tank
0.0288 MGD
331
Anode Cleaning Sewer Line
0.0288 MGD
332
Heat Exchanger Condensate
0.0336 MGD
333
Stormwater
334
Pump Seal Water Cell House
0.02736 MGD
324
Pump Seal Water Leach
0.0118 MGD
329
Pump Seal Water Purification
0.0072 MGD
330
Equalization Pond
325
Neutralization with Lime
Clarifier
326
0.472 MGD
Polishing Lagoon
327
0.475 MGD
Discharge

FIGURE V-7

SAMPLING SITES AT PRIMARY ZINC PLANT G

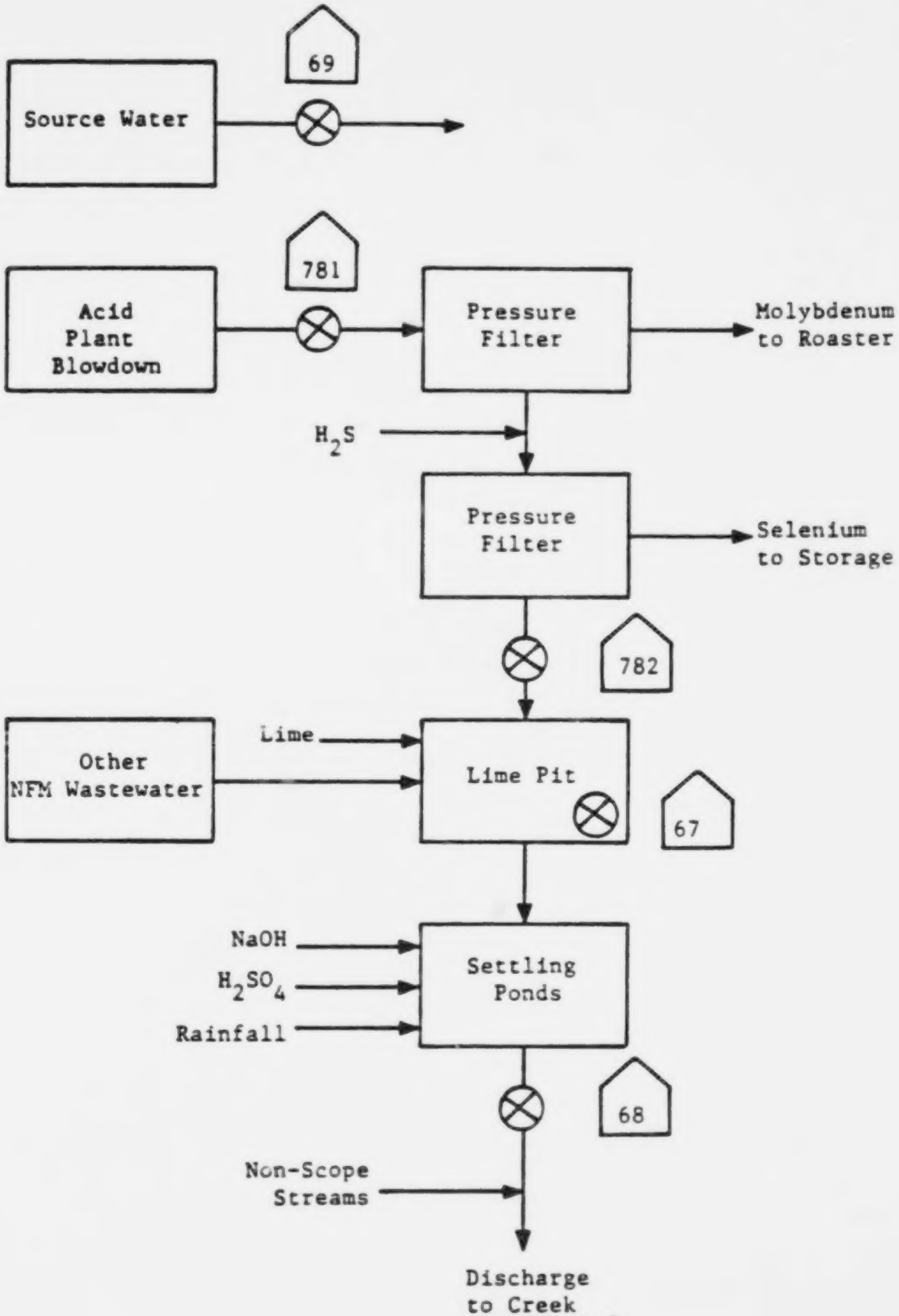
69
Source Water
781
Acid Plant Blowdown
Pressure Filter
Molybdenum to Roaster
H_2S
Pressure Filter
Selenium to Storage
782
Lime
Other NFM Wastewater
Lime Pit
67
NaOH
H_2SO_4
Rainfall
Settling Ponds
68
Non-Scope Streams
Discharge to Creek

FIGURE V-8

SAMPLING SITES AT PRIMARY MOLYBDENUM PLANT B

SECTION VI

SELECTION OF POLLUTANTS

This section examines chemical analysis data presented in Section V and discusses the selection or exclusion of pollutants for potential limitation. Each pollutant selected for potential limitation is discussed in Section VI of Vol. 1. That discussion provides information about where the pollutant originates (i.e., whether it is a naturally occurring substance, processed metal, or a manufactured compound); toxic effects of the pollutant in humans and other animals; and behavior of the pollutant in POTW at the concentrations expected in industrial discharges.

The discussion that follows describes the analysis that was performed to select or exclude pollutants for further consideration for limitations and standards. Pollutants will be selected for further consideration if they are present in concentrations treatable by the technologies considered in this analysis. The treatable concentrations used for the priority metals were the long-term performance values achievable by lime precipitation, sedimentation, and filtration. The treatable concentrations used for the priority organics were the long-term performance values achievable by carbon adsorption.

As discussed in Section V, EPA collected wastewater characterization data from several plants, during the rulemaking process. The waste streams sampled were from acid plants associated with all four metal types. The same pollutants selected for further consideration for limitation at proposal have been selected for promulgation with the addition of the nonconventional pollutants fluoride and molybdenum for molybdenum acid plants only.

CONVENTIONAL AND NONCONVENTIONAL POLLUTANT PARAMETERS

This study examined samples from metallurgical acid plants for three conventional pollutant parameters (oil and grease, total suspended solids, and pH) and the nonconventional pollutant parameters fluoride and molybdenum.

CONVENTIONAL AND NONCONVENTIONAL POLLUTANT PARAMETERS SELECTED

The conventional and nonconventional pollutant parameters selected for limitation in this subcategory are as follows:

Molybdenum (for molybdenum acid plants only)
Fluoride (for molybdenum acid plants only)
Total suspended solids (TSS)
pH

Molybdenum was detected in all four samples of acid plant blowdown collected at a primary molybdenum roasting facility. The observed concentrations range from 1.69 to 8.38 mg/l. The Agency also received extensive data with comments submitted on the nonferrous metals manufacturing rulemaking which show that molybdenum may typically be present in molybdenum acid plant blowdown in concentrations as high as 80 mg/l. Because these concentrations are significantly higher than the level achievable with available treatment, molybdenum is selected for limitation in this subcategory for molybdenum acid plants only. See Section X for a discussion on the treatment effectiveness level for molybdenum.

Fluoride was detected in all three samples of acid plant blowdown collected at a primary molybdenum roasting facility. The observed concentrations ranged from 25 to 720 mg/l. Because these concentrations are significantly higher than the 14.5 mg/l achievable with available treatment, fluoride is selected for limitation in this subcategory for molybdenum acid plants only.

The total suspended solids concentration in 11 samples ranged from 10 to 23,740 mg/l. All of these values are above the 2.6 mg/l concentration attainable by available treatment. Furthermore, most of the methods used to remove toxic metals do so by converting these metals to precipitates. Meeting a limitation on total suspended solids also ensures that sedimentation to remove precipitated toxic metals has been effective. For these reasons, total suspended solids are selected for further consideration for limitation.

Acid plant wastewater varied widely in pH, from 0.6 to 11.5. Many harmful effects may be caused by extreme pH values, or by rapid changes in pH. Therefore, pH is selected for further consideration for limitation.

PRIORITY POLLUTANTS

The frequency of occurrence of the priority pollutants in the raw wastewater samples taken is presented in Table VI-3 (page 1400). The raw wastewater samples from five streams 88, 89, 209, 212, 321, and 781 are considered in the frequency of occurrence count. These streams contain raw wastewater from processes associated with the metallurgical acid plants subcategory and include the data collected by the Agency after proposal at one primary zinc metallurgical acid plant and one primary molybdenum acid plant. Other streams from which raw wastewater was sampled contained acid plant wastewater, however these streams also contained wastewater associated with other subcategories (lead, copper, or zinc). These samples are not considered in the frequency of occurrence count. The data in the frequency of occurrence table provide the basis for the consideration of specific pollutants, as discussed below.

PRIORITY POLLUTANTS NEVER DETECTED

The priority pollutants listed in Table VI-1 (page 1396) were not detected in any wastewater samples from this subcategory; therefore, they are not selected for consideration in establishing limitations.

PRIORITY POLLUTANTS NEVER FOUND ABOVE THEIR ANALYTICAL QUANTIFICATION CONCENTRATION

The priority pollutants listed in Table VI-2 (page 1398) were never found above their analytical quantification concentration in any wastewater samples from this subcategory; therefore, they are not selected for consideration in establishing limitations.

PRIORITY POLLUTANTS PRESENT BELOW CONCENTRATIONS ACHIEVABLE BY TREATMENT

Beryllium and cyanide are not selected for consideration in establishing limitations because they were not found in any wastewater samples from this subcategory above concentrations considered achievable by existing or available treatment technologies.

Beryllium was found above its analytical quantification concentration in two of 15 samples with concentrations of 0.01 mg/l and 0.002 mg/l. Both of these values are below the 0.20 mg/l treatable concentration. Therefore, beryllium is not selected for limitation.

Cyanide was found above its analytical quantification concentration in two of 13 samples with concentrations of 0.033 mg/l and 0.032 mg/l. Because both of these values are below the treatable concentration of 0.047 mg/l, cyanide is not selected for limitation.

PRIORITY POLLUTANTS DETECTED IN A SMALL NUMBER OF SOURCES

The pollutants listed below were found in only a small number of sources within the subcategory and their occurrence is uniquely related to only those sources. Therefore, the following pollutants were not selected for limitation in this subcategory.

6. carbon tetrachloride
13. 1,1-dichloroethane
22. parachlorometa-cresol
23. chloroform
38. ethylbenzene
44. methylene chloride
66. bis(2-ethylhexyl) phthalate
78&81. anthracene&phenanthrene
85. tetrachloroethylene
86. toluene
127. thallium

Although these pollutants were not selected for consideration in establishing nationwide limitations, it may be appropriate, on a case-by-case basis, for the local permit writer to specify effluent limitations.

Carbon tetrachloride was present above its treatable concentration in two of 11 samples collected from three plants. Because it was detected at only one plant, indicating the pollutant is probably site-specific, carbon tetrachloride is not selected for limitation.

1,1-Dichloroethane was found above its analytical quantification concentration in just one of 11 samples collected at three plants. The reported concentration, 0.18 mg/l, is above 0.01 mg/l, which is considered achievable by available treatment. Because it was found at only one plant, indicating the pollutant is probably site-specific, 1,1-dichloroethane is not selected for limitation.

Parachlorometa-cresol was detected above its treatable concentration in two of five samples collected. The reported concentrations were 0.045 mg/l and 0.042 mg/l. Both samples containing parachlorometa-cresol were from the same acid plant blowdown raw wastewater stream. Two other streams did not contain this pollutant. Therefore, this pollutant is considered site-specific so it is not selected for limitation.

Chloroform was found above its treatable concentration in two of 11 samples. This pollutant was detected in six other samples below the analytical quantification level. Chloroform, a common laboratory solvent, is not attributable to specific materials or processes associated with acid plants. Since the possibility of sample contamination is likely, chloroform is not selected for limitation.

Ethylbenzene was detected in only one of 11 samples collected from three plants. The value reported was 0.049 mg/l. Because it was treatable in only one sample, indicating the pollutant is probably site-specific, ethylbenzene is not selected for limitation.

Methylene chloride was found above its treatable concentration in three of 11 samples, at concentrations of 0.016, 0.224, and 0.23 mg/l. This pollutant is not attributable to specific materials or processes associated with acid plants; however. it is a common solvent used in analytical laboratories. Since the possibility of sample contamination is likely, methylene chloride is not selected for limitation.

Dichlorobromomethane was found in only one of 11 samples. The detected concentration, 0.014 mg/l, is slightly above the treatable concentration. Also, dichlorobromomethane was not found in two other samples from the same stream. Since it was found in only one of five raw wastewater streams sampled, it can be considered site-specific. For these reasons, this pollutant is not selected for limitation.

Bis(2-ethylhexyl) phthalate was found above its analytical quantification concentration in six of 11 samples. The maximum concentration observed was 0.193 mg/l. The presence of this pollutant is not attributable to materials or processes associated with the metallurgical acid plant subcategory. It is commonly used as a plasticizer in laboratory and field sampling equipment. EPA suspects sample contamination as the source of this pollutant. Therefore, bis(2-ethylhexyl) phthalate is not selected for limitation.

Anthracene and phenanthrene (analyzed together for eight samples) were found above their analytical quantification concentrations in one of 11 samples collected from three plants. The single sample was also above the treatable concentration (0.010 mg/l). Since they were treatable in only one sample, indicating that these pollutants are probably site-specific, anthracene and phenanthrene are not selected for limitation.

Tetrachloroethylene was detected in six of 11 samples collected from three plants. Five of the six samples had concentrations below the analytical quantification limit. The reported concentration was 0.011 mg/l, which is slightly above the treatable concentration. Therefore, tetrachloroethylene is not selected for limitation.

Toluene was found above its analytical quantification concentration in only one of 11 samples. The reported toluene concentration, 0.057 mg/l, is above 0.010 mg/l, which is considered achievable by available treatment. However because it was found at only one plant, indicating the pollutant is site-specific, toluene is not selected for limitation.

Thallium was found above its analytical quantification concentration in three of 15 samples. In only two of the samples was the thallium concentration above its treatable concentration of 0.34 mg/l, and these two were both in the same stream at only one plant. Therefore, thallium is not selected for limitation.

TOXIC POLLUTANTS SELECTED FOR CONSIDERATION IN ESTABLISHING LIMITATIONS

The toxic pollutants listed below were selected for further consideration in establishing limitations for this subcategory. The toxic pollutants selected are each discussed following the list.

114. antimony
115. arsenic
118. cadmium
119. chromium
120. copper
122. lead
123. mercury
124. nickel
125. selenium
126. silver

128. zinc

Antimony was detected above its treatable concentration (0.47 mg/l) in four of 15 samples, ranging from 3.4 to 51 mg/l. Therefore, antimony is selected for further consideration for limitation.

Arsenic was found in concentrations above its treatable concentration (0.34 mg/l) in 10 of 15 samples ranging from 1.5 to 4,300 mg/l. Therefore, arsenic is selected for further consideration for limitation.

Cadmium was found in concentrations above its treatable concentration (0.049 mg/l) in 10 of 15 samples ranging from 0.7 to 42.13 mg/l. Therefore, cadmium is selected for further consideration for limitation.

Chromium was found in concentrations above its treatable concentration (0.07 mg/l) in seven of 15 samples ranging from 0.09 to 13.0 mg/l. Therefore, chromium is selected for further consideration for limitation.

Copper was found in concentrations above its treatable concentration (0.39 mg/l) in 12 out of 15 samples ranging from 1.5 to 500 mg/l. Therefore, copper is selected for further consideration for limitation.

Lead was found in concentrations above its treatable concentration (0.08 mg/l) in all 15 samples ranging from 0.4 to 400 mg/l. Therefore, lead is selected for further consideration for limitation.

Mercury was found in concentrations above its treatable concentration (0.036 mg/l) in seven of 15 samples ranging from 0.064 to 2.8 mg/l. Therefore, mercury is selected for further consideration for limitation.

Nickel was found in concentrations above its treatable concentration (0.22 mg/l) in seven of 15 samples ranging from 0.6 to 4.60 mg/l. Therefore, nickel is selected for further consideration for limitation.

Selenium was found in concentrations above its treatable concentration (0.007 mg/l) in eight of 14 samples ranging from 0.29 to 61.2 mg/l. Therefore, selenium is selected for further consideration for limitation.

Silver was found in concentrations above its treatable concentration (0.07 mg/l) in six of 15 samples ranging from 0.09 to 4.9 mg/l. Therefore, silver is selected for further consideration for limitation.

Zinc was found in concentrations above its treatable concentration (0.23 mg/l) in 12 out of 15 samples ranging from 2.35 to 512 mg/l. Therefore, zinc is selected for further consideration for limitation.

TABLE VI-1

TOXIC POLLUTANTS NEVER DETECTED

2. acrolein
3. acrylonitrile
5. benzidene
7. chlorobenzene
8. 1,2,4-trichlorobenzene
9. hexachlorobenzene
12. hexachloroethane
16. chloroethane
17. DELETED
18. bis (2-chloroethyl) ether
19. 2-chloroethyl vinyl ether (mixed)
20. 2-chloronaphthalene
21. 2,4.6-trichlorophenol
24. 2-chlorophenol
25. 1,2-dichlorobenzene
26. 1,3-dichlorobenzene
27. 1,4-dichlorobenzene
28. 3,3'-dichlorobenzidine
30. 1,2-trans-dichloroethylene
31. 2,4-dichlorophenol
32. 1,2-dichloropropane
33. 1,3-dichloropropylene
35. 2,4-dinitrotoluene
36. 2,6-dinitrotoluene
37. 1,2-diphenylhydrazine
40. 4-chlorophenyl phenyl ether
41. 4-bromophenyl phenyl ether
42. bis(2-chloroisopropyl) ether
43. bis(2-chloroethoxy) methane
45. methyl chloride
46. methyl bromide
50. DELETED
52. hexachlorobutadiene
53. hexachlorocyclopentadiene
57. 2-nitrophenol
58. 4-nitrophenol
59. 2,4-dinitrophenol
60. 4,6-dinitro-o-cresol
61. N-nitrosodimethylamine
63. N-nitrosodi-n-propylamine
72. benzo(z)anthracene
77. acenaphthylene
79. benzo(ghi)perylene

TABLE VI-1 (Continued)

TOXIC POLLUTANTS NEVER DETECTED

82. dibenzo(a,h)anthracene
83. indeno(1,2,4-cd)pyrene
88. vinyl chloride
89. aldrin
95. alpha-endosulfan
97. endosulfan sulfate
113. toxaphene
116. asbestos
129. 2,3,7,8-tetrachlorodibenzo-p-dioxin

TABLE VI-2

TOXIC POLLUTANTS NEVER FOUND ABOVE THEIR ANALYTICAL QUANTIFICATION CONCENTRATION

1. acenaphthene
4. benzene
10. 1,2-dichloroethane
11. 1,1,1-trichloroethane
14. 1,1,2-trichloroethane
15. 1,1,2,2-tetrachloroethane
29. 1,1-dichloroethylene
34. 2,4-dimethylphenol
39. fluoranthene
47. bromoform
49. DELETED
51. chlorodibromomethane
54. isophorone
55. naphthalene
56. nitrobenzene
62. N-nitrosodiphenylamine
64. pentachlorophenol
65. phenol
67. butyl benzyl phthalate
68. di-n-butyl phthalate
69. di-n-octyl phthalate
70. diethyl phthalate
71. dimethyl phthalate
73. benzo(a)pyrene (3,4-benzopyrene)
74. 3,4-benzofluoranthene
75. benzo(k)fluoranthene (11,12-benzofluoranthene)
76. chrysene
80. fluorene
84. pyrene
87. trichloroethylene
90. dieldrin
91. chlordane (technical mixture and metabolites)
92. 4,4'-DDT
93. 4,4'-DDE(p,p'DDX)
94. 4,4'-DDD(p,p'TDE)
96. b-endosulfan-Beta
98. endrin
99. endrin aldehyde
100. heptachlor
101. heptachlor epoxide

TABLE VI-2 (Continued)

TOXIC POLLUTANTS NEVER FOUND ABOVE THEIR ANALYTICAL QUANTIFICATION CONCENTRATION

102. a-BHC-Alpha
103. b-BHC-Beta
104. r-BHC (lindane)-Gamma
105. delta-BHC
106. PCB-1242 (Arochlor 1242) (a)
107. PCB-1254 (Arochlor 1254) (a)
108. PCB 1221 (Arochlor 1221) (a)
109. PCB-1232 (Arochlor 1232) (b)
110. PCB-1248 (Arochlor 1248) (b)
111. PCB-1260 (Arochlor 1260) (b)
112. PCB-1016 (Arochlor 1016) (b)

(a), (b) Reported together

Table VI-1

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
METALLURGICAL ACID PLANTS
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	Not Detected	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
1. acenaphthene	0.010	0.010	5	11	10	1		
2. acrolein	0.010	0.010	5	11	11			
3. acrylonitrile	0.010	0.010	5	11	11			
4. benzene	0.010	0.010	5	11	7	4		
5. benzidine	0.010	0.010	5	11	11			
6. carbon tetrachloride	0.010	0.010	5	11	8	1		2
7. chlorobenzene	0.010	0.010	5	11	11			
8. 1,2,4-trichlorobenzene	0.010	0.010	5	11	11			
9. hexchlorobenzene	0.010	0.010	5	11	11			
10. 1,2-dichloroethane	0.010	0.010	5	11	10	1		
11. 1,1,1-trichloroethane	0.010	0.010	5	11	8	3		
12. hexachloroethane	0.010	0.010	5	11	11			
13. 1,1-dichloroethane	0.010	0.010	5	11	10			1
14. 1,1,2-trichloroethane	0.010	0.010	5	11	10	1		
15. 1,1,2,2-tetrachloroethane	0.010	0.010	5	11	9	2		
16. chloroethane	0.010	0.010	5	11	11			
17. bis(chloromethyl)ether	0.010	0.010	5	11	11			
18. bis(2-chloroethyl)ether	0.010	0.010	5	11	11			
19. 2-chloroethyl vinyl ether	0.010	0.010	5	11	11			
20. 2-chloronaphthalene	0.010	0.010	5	11	11			
21. 2,4,6-trichlorophenol	0.010	0.010	3	5	5			
22. parachlorometa cresol	0.010	0.010	3	5	2	1		2
23. chloroform	0.010	0.010	5	11	3	6		2
24. 2-chlorophenol	0.010	0.010	2	4	4			
25. 1,2-dichlorobenzene	0.010	0.010	5	11	11			
26. 1,3-dichlorobenzene	0.010	0.010	5	11	11			
27. 1,4-dichlorobenzene	0.010	0.010	5	11	11			
28. 3,3'-dichlorobenzidine	0.010	0.010	5	11	11			
29. 1,1-dichloroethylene	0.010	0.010	5	11	10	1		
30. 1,2-trans-dichloroethylene	0.010	0.010	5	11	11			
31. 2,4-dichlorophenol	0.010	0.010	3	5	5			
32. 1,2-dichloropropane	0.010	0.010	5	11	11			
33. 1,3-dichloropropylene	0.010	0.010	5	11	11			

Table VI-1 (Continued)

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
METALLURGICAL ACID PLANTS
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	Not Detected	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
34. 2,4-dimethylphenol	0.010	0.010	3	5	3	2		
35. 2,3-dinitrotoluene	0.010	0.010	5	11	11			
36. 2,6-dinitrotoluene	0.010	0.010	5	11	11			
37. 1,2-diphenylhydrazine	0.010	0.010	5	11	11			
38. ethylbenzene	0.010	0.010	5	11	10			1
39. fluoranthene	0.010	0.010	5	11	8	3		
40. 4-chlorophenyl phenyl ether	0.010	0.010	5	11	11			
41. 4-bromophenyl phenyl ether	0.010	0.010	5	11	11			
42. bis(2-chloroisopropyl)ether	0.010	0.010	5	11	11			
43. bis(2-chloroethoxy)methane	0.010	0.010	5	11	11			
44. methylene chloride	0.010	0.010	5	11	6	2		3
45. methyl chloride	0.010	0.010	5	11	11			
46. methyl bromide	0.010	0.010	5	11	11			
47. bromoform	0.010	0.010	5	11	9	2		
48. dichlorobromomethane	0.010	0.010	5	11	10			1
49. trichlorofluoromethane	0.010	0.010	5	11	10	1		
50. dichlorodifluoromethane	0.010	0.010	5	11	11			
51. chlorodibromomethane	0.010	0.010	5	11	10	1		
52. hexachlorobutadiene	0.010	0.010	5	11	11			
53. hexachlorocyclopentadiene	0.010	0.010	5	11	11			
54. isophorone	0.010	0.010	5	11	10	1		
55. naphthalene	0.010	0.010	5	11	9	2		
56. nitrobenzene	0.010	0.010	5	11	10	1		
57. 2-nitrophenol	0.010	0.010	3	5	5			
58. 4-nitrophenol	0.010	0.010	3	5	5			
59. 2,4-dinitrophenol	0.010	0.010	3	5	5			
60. 4,6-dinitro-o-cresol	0.010	0.010	3	5	5			
61. N-nitrosodimethylamine	0.010	0.010	5	11	11			
62. N-nitrosodiphenylamine	0.010	0.010	5	11	9	2		
63. N-nitrosodi-n-propylamine	0.010	0.010	5	11	11			
64. pentachlorophenol	0.010	0.010	2	4	3	1		
65. phenol	0.010	0.010	2	4	2	2		

Table VI-13 (Continued)

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
METALLURGICAL ACID PLANTS
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/l)(a)	Treatable Concentration (mg/l)(b)	Number of Streams Analyzed	Number of Samples Analyzed	Not Detected	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
66. bis(2-ethylhexyl)phthalate	0.010	0.010	5	11	1	4	1	5
67. butyl benzyl phthalate	0.010	0.010	5	11	8	3		
68. di-n-butyl phthalate	0.010	0.010	5	11	5	6		
69. di-n-octyl phthalate	0.010	0.010	5	11	8	3		
70. diethyl phthalate	0.010	0.010	5	11	10	1		
71. dimethyl phthalate	0.010	0.010	5	11	9	2		
72. benzo(a)anthracene	0.010	0.010	5	11	11			
73. benzo(a)pyrene	0.010	0.010	5	11	8	3		
74. 3,4-benzofluoranthene	0.010	0.010	5	11	10	1		
75. benzo(k)fluoranthene	0.010	0.010	5	11	10	1		
76. chrysene	0.010	0.010	5	11	8	3		
77. acenaphthylene	0.010	0.010	5	11	11			
78. anthracene (c)	0.010	0.010	5	11	6	4		1
79. benzo(ghi)perylene	0.010	0.010	5	11	11			
80. fluorene	0.010	0.010	5	11	10	1		
81. phenanthrene (c)	0.010	0.010	1	11	6	4		1
82. dibenzo(a,h)anthracene	0.010	0.010	5	11	11			
83. ideno(1,2,3-cd)pyrene	0.010	0.010	5	11	11			
84. pyrene	0.010	0.010	5	11	6	5		
85. tetrachloroethylene	0.010	0.010	5	11	5	5		1
86. toluene	0.010	0.010	5	11	9	1		1
87. trichloroethylene	0.010	0.010	5	11	6	5		
88. vinyl chloride	0.010	0.010	5	11	11			
89. aldrin	0.005	0.010	4	10	10			
90. dieldrin	0.005	0.010	4	10	5	5		
91. chlordane	0.005	0.010	4	10	6	4		
92. 3,3'DDT	0.005	0.010	4	10	5	5		
93. 4,4'-DDE	0.005	0.010	4	10	6	4		
94. 4,4'-DDD	0.005	0.010	4	10	8	2		
95. alpha-endosulfan	0.005	0.010	4	10	10			
96. beta-endosulfan	0.005	0.010	4	10	9	1		
97. endosulfan sulfate	0.005	0.010	4	10	10			

Table VI-13 (Continued)

FREQUENCY OF OCCURRENCE OF TOXIC POLLUTANTS
METALLURGICAL ACID PLANTS
RAW WASTEWATER

Pollutant	Analytical Quantification Concentration (mg/1)(a)	Treatable Concentration (mg/1)(b)	Number of Streams Analyzed	Number of Samples Analyzed	Not Detected	Detected Below Quantification Concentration	Detected Below Treatable Concentration	Detected Above Treatable Concentration
98. endrin	0.005	0.010	4	10	7	3		
99. endrin aldehyde	0.005	0.010	4	10	5	5		
100. heptachlor	0.005	0.010	4	10	4	6		
101. heptachlor epoxide	0.005	0.010	4	10	5	5		
102. alpha-BHC	0.005	0.010	4	10	9	1		
103. beta-BHC	0.005	0.010	4	10	2	8		
104. gamma-BHC	0.005	0.010	4	10	7	3		
105. delta-BHC	0.005	0.010	4	10	9	1		
106. PCB-1242 (d)	0.005	0.010	4	10	4	6		
107. PCB-1254 (d)	0.005	0.010	1	10	4	6		
108. PCB-1221 (d)	0.005	0.010	1	10	4	6		
109. PCB-1232 (e)	0.005	0.010	4	10	4	6		
110. PCB-1243 (e)	0.005	0.010	1	10	4	6		
111. PCB-1260 (e)	0.005	0.010	1	10	4	6		
112. PCB-1016 (e)	0.005	0.010	1	10	4	6		
113. toxaphene	0.005	0.010	4	10	10			
114. antimony	0.100	0.470	5	11	6		1	4
115. arsenic	0.010	0.340	5	11	4		1	6
116. asbestos	10 MFL	10 MFL	NOT ANALYZED					
117. beryllium	0.010	0.200	5	11	9	2		
118. cadmium	0.002	0.049	5	11	1			10
119. chromium	0.005	0.070	5	11	4		4	3
120. copper	0.009	0.390	5	11				11
121. cyanide	0.02	0.047	5	11	4	7		
122. lead	0.020	0.080	5	11				11
123. mercury	0.0001	0.036	5	11	2		2	7
124. nickel	0.005	0.220	5	11	3		5	3
125. selenium	0.01	0.200	5	10	2		4	4
126. silver	0.02	0.070	5	11			5	6
127. thallium	0.100	0.340	5	11	8		1	2
128. zinc	0.050	0.230	5	11				11
129. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	NOT ANALYZED							

(a) Analytical quantification concentration was reported with data (see Section V).

(b) Treatable concentrations are based on performance of lime precipitation, sedimentation, and filtration for toxic metal pollutants and based on activated carbon adsorption for toxic organic pollutants.

(c) Reported together for eight samples.

(d), (e) Reported together

(f) Analytical quantification concentration for EPA Method 335.2, Total Cyanide Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

The preceding sections of this supplement discussed the sources, flows, and characteristics of metallurgical acid plant wastewater. This section gives the technical basis for the existing BPT effluent limitations, indicates the treatment technologies which are currently practiced, and summarizes the treatment options which have been examined as part of this analysis.

TECHNICAL BASIS OF BPT

As mentioned in Section III, EPA promulgated best practicable control technology currently available (BPT) effluent limitations guidelines for the metallurgical acid plants subcategory of the nonferrous metals category on July 2, 1980. The technology basis for the 1980 BPT effluent limitations was treatment of acid plant wastewater by precipitation and flocculation with lime and polymers, followed by sedimentation.

The production normalizing parameter for the 1980 BPT was tons of 100 percent H_2SO_4 capacity (rather than production). The BPT wastewater flow rate was determined to be 6,079 l/kkg (1,457 gal/ton) at 100 percent equivalent sulfuric acid capacity.

The 1980 BPT effluent limitations applied only to metallurgical acid plants associated with primary copper plants. Also, the pollutants selected for regulation were TSS, copper, cadmium, lead, zinc, and pH. As discussed in Section VI, additional pollutants are now considered for limitation in the revised limitations and standards.

The only change to the promulgated BPT limitations for the metallurgical acid plants subcategory is the inclusion of sulfuric acid plants associated with primary lead, primary molybdenum, and primary zinc plants. Also, limitations for the pollutants molybdenum and fluoride are added for molybdenum acid plants only and iron co-precipitation is included as part of the BPT technology basis for molybdenum acid plants to control discharges of molybdenum. As with primary copper acid plants, associated wastewater generated by air pollution control (or gas conditioning systems) for sulfur dioxide off-gases from pyrometallurgical operations at these plants are also included as part of the acid plant blowdown.

CURRENT CONTROL AND TREATMENT PRACTICES

As described in Section III, there are 22 metallurgical acid plants associated with primary copper, primary lead, primary molybdenum, and primary zinc plants in the U.S. Ten acid plants are associated with primary copper plants, three are associated

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with primary lead plants, three are associated with primary molybdenum plants, and six are associated with primary zinc plants.

In these primary metals plants, the metals are usually produced from sulfide ores. In the production sequence, sulfur oxides are released in the pyrometallurgical processes of roasting, sintering, smelting, or converting.

After the hot gases have been subjected to waste heat recovery and primary particulate control, the gases are usually treated with an open scrubbing tower (or one scrubber performing both operations of preconditioning and scrubber) and a mist precipitator (for final particulate and SO_3 removal). Due to a build-up of salts in the scrubbing liquor, a blowdown may be necessary.

In areas of net evaporation, this wastewater is usually impounded and evaporated. Other control measures are reuse and minimization of the amount of blowdown. Four plants indicated cooling towers were used in treating acid plant blowdown. Although the functions of these cooling towers in the treatment systems were not indicated, many of the plants may be using cooling towers to cool the wastewater stream prior to reuse or discharge. Some plants may be concentrating the wastewater stream with their cooling towers.

Using the acid plant blowdown for cooling hot gases from other processes, feeding the blowdown into fluid bed roasters, or using the blowdown for ore concentrating are three possible reuse schemes. One plant reports that it uses its blowdown for ore concentrating after sedimentation. The amount of acid plant blowdown can be minimized by using efficient primary particulate control devices. This minimizes the load carried to acid plant scrubbers, thus minimizing required blowdown.

As discussed in Section V, wastewater associated with metallurgical acid plants subcategory is characterized by the presence of the toxic metal pollutants and suspended solids. The raw (untreated) wastewater data for specific sources as well as combined waste streams is presented in Section V. Generally, these pollutants are present in each of the waste streams at treatable concentrations, so these waste streams are commonly combined for treatment to reduce the concentrations of these pollutants. Construction of one wastewater treatment system for combined treatment allows plants to take advantage of economies of scale and, in some instances, to combine streams of differing alkalinity to reduce treatment chemical requirements. Ten plants in this subcategory currently have combined wastewater treatment systems, nine have lime precipitation and sedimentation, and two have lime precipitation, sedimentation, and filtration. One of the plants with lime precipitation and sedimentation has preliminary treatment consisting of sulfide addition and filtration. As such, three options have been considered for the promulgated BAT, BDT, and pretreatment in this subcategory, based on combined treatment of these compatible waste streams.

CONTROL AND TREATMENT OPTIONS

Based on an examination of the wastewater sampling data, three control and treatment technologies that effectively control the pollutants found in metallurgical acid plants smelting wastewaters were selected for evaluation for copper, lead, zinc, and molybdenum metallurgical acid plants since proposal. On March 18, 1985, the Agency published a Notice of Data Availability which revised the three proposed options to include iron coprecipitation for molybdenum acid plants to achieve discharge limitations for molybdenum. These technology options are discussed below. Other treatment technologies considered at proposal include activated alumina adsorption (Option D) and activated carbon adsorption (Option E). These technologies were not selected for evaluation because they are not applicable to the metallurgical acid plants subcategory. Although arsenic was found in process wastewaters at treatable concentrations, activated alumina technology was not selected because it is not demonstrated in the nonferrous metals manufacturing category, nor is it clearly transferable. Since no toxic organic pollutants were selected for consideration for limitation in this subcategory, activated carbon technology is not applicable.

OPTION A

Option A for the metallurgical acid plants subcategory is equivalent to the BPT control and treatment technologies. The BPT end-of-pipe treatment scheme consists of chemical precipitation and sedimentation. Iron co-precipitation is also included for molybdenum acid plants. This technology is included to control discharges of molybdenum. Chemical precipitation and sedimentation consists of lime addition to precipitate metals followed by gravity sedimentation for the removal of suspended solids, including the metal precipitates.

OPTION B

Option B for the metallurgical acid plants subcategory consists of all the requirements of Option A (lime precipitation and sedimentation) plus in-plant reduction of process wastewater flow. Iron co-precipitation is also included for molybdenum acid plants. This technology is included to control discharges of molybdenum. Water recycle is the control mechanism for flow reduction.

OPTION C

Option C for the metallurgical acid plants subcategory consists of Option B (lime precipitation, sedimentation, and in-process flow reduction) with the addition of sulfide precipitation, and multimedia filtration. The technology basis for the one primary copper plant and all primary molybdenum plants is in-process flow reduction, sulfide precipitation, pressure filtration, lime precipitation, sedimentation, and multimedia filtration. Iron co-precipitation is also part of the technology basis for primary molybdenum acid plants. This technology is included to control discharges of molybdenum. For the zinc and lead plants, the technology basis is in-process flow reduction, lime precipitation and sedimentation, sulfide precipitation and sedimentation, and multimedia filtration.

Multimedia filtration is used to remove suspended solids, including precipitated metals, below the level attainable by gravity sedimentation. The model filter is of the gravity, mixed-media type, although other forms of filters such as rapid sand filters or pressure filters would perform satisfactorily. The addition of filters also provides for consistent removal during periods of time when there are rapid increases in flows or loadings of pollutants to the treatment system.

SECTION VIII

COSTS, ENERGY, AND NONWATER QUALITY ASPECTS

This section describes the method used to develop the costs associated with the control and treatment technologies discussed in Section VII for wastewaters from metallurgical acid plants. The energy requirements of the considered options as well as solid waste and air pollution aspects are also discussed.

In Section VI of this supplement, several pollutants and pollutant parameters are selected for further consideration for limitation for the metallurgical acid plants subcategory. These pollutants or pollutant parameters include several toxic metals, total suspended solids, and pH. Metals are most economically removed by chemical precipitation, sedimentation, and filtration. The recycle of acid plant blowdown through holding tanks or cooling towers may also be added as a preliminary flow reduction measure which decreases the discharge flow and results in the concentration of pollutants in the effluent stream. Treatment of a more concentrated effluent introduces the possible economic benefits associated with treating a lower volume of wastewater.

TREATMENT OPTIONS COSTED FOR EXISTING SOURCES

As discussed in Section III of this supplement, metallurgical acid plants are located on-site at primary copper, lead, molybdenum, and zinc smelters. Three treatment options have been considered for promulgation for the metallurgical acid plants subcategory. These options are summarized below and are schematically presented in Figures X-1 through X-4 (pages 1431 - 1434).

OPTION A

Option A for the metallurgical acid plant subcategory consists of lime precipitation and sedimentation end-of-pipe treatment technology. Iron co-precipitation is included in Option A for molybdenum acid plants. This technology is included to control discharges of molybdenum.

OPTION B

Option B for the metallurgical acid plant subcategory requires flow reduction measures consisting of the recycle of acid plant blowdown through holding tanks or cooling towers if cooling is required, and end-of-pipe treatment consisting of lime precipitation and sedimentation, and iron co-precipitation for molybdenum acid plants.

OPTION C

Option C for the metallurgical acid plant subcategory requires flow reduction measures consisting of the recycle of acid plant blowdown through holding tanks and cooling towers, and end-of-pipe treatment technology consisting of lime precipitation and sedimentation, sulfide precipitation, iron co-precipitation for molybdenum acid plants, and multimedia filtration.

Cost Methodology

A detailed discussion of the methodology used to develop the compliance costs is presented in Section VIII of Vol. 1. Plant-by-plant compliance costs have been estimated for the nonferrous metals manufacturing category and are presented in the administrative record supporting this regulation. The costs developed for the final regulation are presented in Tables VIII-1 and VIII-2 (page 1414) for the direct and indirect dischargers, respectively.

Each of the major assumptions used to develop compliance costs is presented in Section VIII of Vol. 1. However, each subcategory contains a unique set of waste streams requiring certain subcategory-specific assumptions to develop compliance costs. Four major assumptions are discussed briefly below.

(1) Flow reduction of the acid plant blowdown is accomplished using cooling towers. Annual costs associated with maintenance and chemicals to prevent biological growth, corrosion, and scale formation are included in the estimated compliance costs. If a plant currently recycles acid plant blowdown, capital costs of the recycle equipment (cooling tower, piping, and pumps) were not included in the compliance costs.

(2) Sludge generated by the sulfide precipitation and sedimentation process at the primary zinc and primary lead facilities was considered hazardous waste for disposal purposes. At the one primary copper facility and all primary molybdenum facilities, sludge generated by the sulfide precipitation and pressure filtration process was also considered hazardous waste.

(3) Because the compliance costs represent incremental costs an acid plant may be expected to incur in complying with this regulation, annual costs for inplace treatment used to comply with promulgated BPT regulations in the primary zinc and primary lead subcategories are also not included in this regulation.

(4) The cost of treating acid plant blowdown from acid plants in the primary copper, primary zinc, and primary lead subcategories is determined by flow-weighting appropriate costs. The entire cost of cooling towers for flow reduction of the acid plant blowdown is attributed to the metallurgical acid plants subcategory. Costs for sulfide precipitation and settle are attributed to the metallurgical acid subcategory for primary copper and

primary lead plants. Sulfide precipitation costs are apportioned between the primary zinc and metallurgical acid subcategories on a flow-weighted basis. Compliance cost estimates for the two primary molybdenum metallurgical acid plants were developed by costing separate treatment systems to treat acid plant blowdown.

NONWATER QUALITY ASPECTS

Nonwater quality impacts specific to the metallurgical acid plants subcategory, including energy requirements, solid waste and air pollution are discussed below.

ENERGY REQUIREMENTS

The methodology used for determining the energy requirements for the various options is discussed in Section VIII of the General Development Document. Energy requirements for the three options considered are estimated at 1,158 MW-hr/yr, 1,158 MW-hr/yr, and 1.746 MW-hr/yr for Options A, B, and C, respectively. Option C represents less than one percent of a typical plant's electrical usage. It is therefore concluded that the energy requirements of the treatment options considered will have no significant impact on total plant energy consumption.

SOLID WASTE

Sludges will necessarily contain additional quantities (and concentrations) of toxic metal pollutants. Wastes generated by primary smelters and refiners are currently exempt from regulation by Act of Congress (Resource Conservation and Recovery Act (RCRA)) Section 3001(b) Consequently, sludges generated from treating primary industries' wastewater, including metallurgical acid plants wastewater, are not presently subject to regulation as hazardous wastes.

The technology basis for the metallurgical acid plants subcategory includes sulfide precipitation for the control of various toxic metals. The Agency believes sludge generated through sulfide precipitation (and sedimentation or pressure filtration) will be classified as hazardous under RCRA. The costs of hazardous waste disposal were considered in the economic analysis for this subcategory (in spite of the current statutory and regulation exemption) because sulfide will not form metal hydroxides that resist leaching. The costs of hazardous waste disposal were determined to be economically achievable. However, lime sludges are not expected to be hazardous. The Agency estimates that the metallurgical acid plants subcategory will generate 544 tons per year of sulfide sludge. Multimedia filtration technology will not result in any significant amount of sludge over that generated by lime precipitation and sulfide precipitation. Implementation of BAT will also result in the generation of 1,270 tons of lime and iron-molybdenum sludge by the two direct discharging molybdenum acid plants. This sludge is considered to be attributable to this rulemaking because there are no existing BPT limitations in place which cover discharge of pollutants from molybdenum acid plants.

If these wastes should be identified or are listed as hazardous, they will come within the scope of RCRA's "cradle to grave" hazardous waste management program, requiring regulation from the point of generation to point of final disposition. EPA's generator standards would require generators of hazardous nonferrous metals manufacturing wastes to meet containerization, labeling, recordkeeping, and reporting requirements; if plants dispose of hazardous wastes off-site, they would have to prepare a manifest which would track the movement of the wastes from the generator's premises to a permitted off-site treatment, storage, or disposal facility. See 40 CFR 262.20 45 FR 33142, May 19 1980) as amended at 45 FR 86973 (December 31, 1980). The transporter regulations require transporters of hazardous wastes to comply with the manifest system to assure that the wastes are delivered to a permitted facility. See 40 CFR 263.20 45 33151 (May 19, 1980), as amended at 45 FR 86973 (December 31, 1980). Finally, RCRA regulations establish standards for hazardous waste treatment, storage, and disposal facilities allowed to receive such wastes. See 40 CFR Part 464 46 FR 2802 (January 12, 1981), 47 FR 32274 (July 26, 1982).

Even if these wastes are not identified as hazardous, they still must be disposed of in compliance with the Subtitle D open dumping standards, implementing 4004 of RCRA. (See 44 FR 53438 September 13, 1979). The Agency has calculated as part of the costs for wastewater treatment the cost of hauling and disposing of these wastes.

AIR POLLUTION

There is no reason to believe that any substantial air pollution will result from implementation of chemical precipitation, sedimentation, sulfide precipitation, and multimedia filtration. These technologies transfer pollutants to solid waste and do not involve air stripping or any other physical process likely to transfer pollutants to air. Minor amounts of sulfur may be emitted during sulfide precipitation, and water vapor containing some particulate matter will be released in the drift from cooling towers, however, the Agency does not consider this impact to be significant.

TABLE VIII-1

COST OF COMPLIANCE FOR THE METALLURGICAL ACID PLANTS SUBCATEGORY

Direct Dischargers
(March, 1982 Dollars)

Option	Capital Cost	Annual Cost
B	1,460,000	1,522,000
C	2,480,000	2,040,000

TABLE VIII-2

COST OF COMPLIANCE FOR THE METALLURGICAL ACID PLANTS SUBCATEGORY

Indirect Dischargers
(March, 1982 Dollars)

Option	Capital Cost	Annual Cost
B	16,100	19,300
C	161,000	84,500

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SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

EPA promulgated BPT effluent limitations for the metallurgical acid plants subcategory on July 2, 1980, as Subpart I of 40 CFR Part 421. The provisions of this subpart apply to process wastewater discharges resulting from or associated with the manufacture of by-product sulfuric acid at primary copper smelters, including any associated air pollution control or gas-conditioning systems for sulfur dioxide off-gases from pyrometallurgical operations. On March 8, 1984, EPA expanded BPT for the metallurgical acid plants subcategory to include sulfuric acid plants associated with primary lead and primary zinc smelting operations as part of the promulgated rulemaking for nonferrous metals manufacturing. The effluent limitations for the lead and zinc acid plants are identical to those promulgated for primary copper acid plants.

EPA has since expanded the applicability of the BPT limitations for metallurgical acid plants to include primary molybdenum acid plants. On March 18, 1985, EPA published a Notice of Data Availability which stated that, in addition to expanding the applicability, EPA was proposing to modify the existing BPT effluent limitations to include limitations for the pollutants molybdenum and fluoride for molybdenum acid plants only.

The effluent limitations established by BPT for the metallurgical acid plants subcategory are based on chemical precipitation and sedimentation treatment technology with the addition of iron coprecipitation preliminary treatment for primary molybdenum acid plants as shown in Figure IX-1 (page 1419). The limitations are based on a production normalized wastewater discharge rate of 6,079 l/kkg of 100 percent sulfuric acid production capacity. The promulgated BPT limitations are shown in Table IX-1 (page 1418).

The Agency has finalized its proposals that metallurgical acid plants at primary lead, primary molybdenum, and primary zinc plants be included in the metallurgical acid plants subcategory originally established for copper smelting acid plants. This new subcategorization is based both on the similarity of acid plant operations (regardless of the metal smelted), and the similarity of the wastewater matrices (confirmed by comparison of raw wastewaters). BPT limitations for the modified metallurgical acid plants subcategory are identical to those already established for primary copper acid plants with the exception that limitations for molybdenum and fluoride are provided for molybdenum acid plants.

The modified BPT effluent limitations have the potential for double counting of zinc acid plants for BPT because EPA is not recommending modification of the primary zinc BPT limitations to eliminate the acid plant portion of those limitations. The justification for this approach is that EPA believes existing permits probably reflect BPT for the combined discharge of zinc smelting and acid plant operations. It is believed that existing permits at these plants will be modified to reflect the BAT requirements where there is no such double counting. Therefore, this apparent inconsistency should not have any actual effect on existing permits. The potential for double counting is not a factor in primary lead because EPA is changing the technology basis for BPT and will eliminate acid plants in the modified BPT. Similarly, all potential double counting of zinc acid plants will be eliminated as part of the recommended BAT, NSPS and PSNS effluent limitations and standards for the primary zinc subcategory.

INDUSTRY COST AND POLLUTANT REMOVAL ESTIMATES

There is no cost associated with expanding the current BPT regulation to include primary zinc and primary lead acid plants because all of the direct discharging primary lead and primary zinc metallurgical acid plants currently have BPT technology in place.

The costs incurred by the two direct discharging primary molybdenum acid plants are not included in this document because they are based on information which has been claimed to be confidential. Implementation of the expanded BPT by the two direct discharging primary molybdenum acid plants would result in the annual removal of 4,432 kilograms of priority metals, 19,687 kilograms of molybdenum, and 27,849 kilograms of fluoride.

TABLE IX-1

BPT EFFLUENT LIMITATIONS FOR THE METALLURGICAL ACID PLANT SUBCATEGORY

Acid Pant Blowdown BPT

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
mg/kg (lb/million lbs) of 100 percent sulfuric acid capacity		
Cadmium	0.180	0.090
Copper	5.000	2 000
Lead	1 800	0.790
Zinc	3.600	0.900
Fluoride[1]	212.800	121.000
Molybdenum[1]	Reserved	Reserved
Total Suspended Solids	304.000	152.000
pH	Within the range of 6.0 to 9.0	

[1] For molybdenum acid plants only.

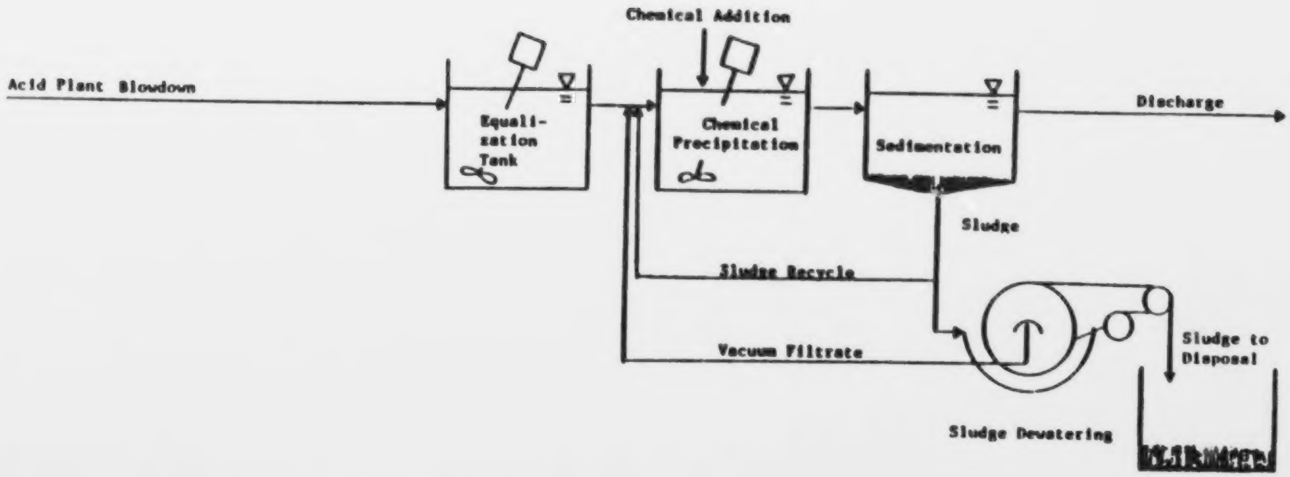
Acid Plant Blowdown
Equalization Tank
Chemical Addition
Chemical Precipitation
Sedimentation
Discharge
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge to Disposal
Sludge Dewatering

FIGURE IX-1
BPT TREATMENT SCHEME OPTION A
METALLURGICAL ACID PLANT SUBCATEGORY

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

The effluent limitations which must be achieved by July 1, 1984, are based on the best control and treatment technology used by a specific point source within the industrial category or subcategory, or by another industry where it is readily transferable. Emphasis is placed on additional treatment techniques applied at the end of the treatment systems currently used for BPT, as well as reduction of the amount of water used and discharged, process control, and treatment technology optimization.

The factors considered in assessing best available technology economically achievable (BAT) include the age of equipment and facilities involved, the process used, process changes, nonwater quality environmental impacts (including energy requirements), and the costs of application of such technology (Section 304 (b) (2)(5) of the Clean Water Act). At a minimum, BAT represents the best available technology economically achievable at plants of various ages, sizes, processes, or other characteristics. Where the Agency has found the existing performance to be uniformly inadequate, BAT may be transferred from a different subcategory or category. BAT may include feasible process changes or internal controls, even when not in common industry practice.

The required assessment of BAT considers costs, but does not require a balancing of costs against effluent reduction benefits (see Weyerhaeuser v. Costle, 590 F.2d 1011 (D.C. Cir. 1978)). However, in assessing the proposed BAT, the Agency has given substantial weight to the economic achievability of the technology.

TECHNICAL APPROACH TO BAT

The Agency reviewed a wide range of technology options and evaluated the available possibilities to ensure that the most effective and beneficial technologies were used as the basis of BAT. To accomplish this, the Agency elected to examine three technology options which could be applied to copper, lead, molybdenum and zinc metallurgical acid plants as BAT options and which would represent substantial progress toward reduction of pollutant discharges above and beyond progress achieved by BPT. On March 18, 1985, the Agency published a Notice of Data Availability which revised the three proposed options to include iron co-precipitation for molybdenum acid plants to control discharges of molybdenum.

In summary, the treatment technologies considered for the metallurgical acid plants subcategory are:

Option A (Figure X-1, page 1431) is based on

- Chemical precipitation and sedimentation
- Iron co-precipitation for molybdenum acid plants

Option B (Figure X-2, page 1432) is based on

- Chemical precipitation and sedimentation
- In-process flow reduction
- Iron co-precipitation for molybdenum acid plants

Option C (Figure X-3, page 1433) is based on

- Chemical precipitation and sedimentation
- In-process flow reduction
- Sulfide precipitation and sedimentation for lead and zinc acid plants
- Sulfide precipitation and pressure filtration preliminary treatment for one copper acid plant and all molybdenum acid plants
- Iron co-precipitation for molybdenum acid plants
- Multimedia filtration

The three options examined for BAT are discussed in greater detail below. The first option considered is the same as the BPT treatment and control technology. The second and third options each represent substantial progress toward the prevention of pollution above and beyond the progress achievable by BPT.

OPTION A

Option A for the metallurgical acid plants subcategory is equivalent to BPT, which includes end-of-pipe treatment of chemical precipitation and sedimentation. Chemical precipitation and sedimentation consists of lime addition to precipitate metals followed by gravity sedimentation for the removal of suspended solids including metal precipitates. Iron co-precipitation is also included for molybdenum acid plants to control discharges of molybdenum (see Figure X-1, page 1431).

OPTION B

Option B for the metallurgical acid plants subcategory consists of all the requirements of Option A (lime precipitation and sedimentation) plus in-plant reduction of process wastewater flow Iron co-precipitation is also included for molybdenum acid plants to control discharges of molybdenum (see Figure X-2, page 1432).

Flow reduction measures, including in-process changes, result in the concentration of pollutants in other effluents. Treatment of a more concentrated effluent allows achievement of a greater net pollutant removal and introduces the possible economic benefits associated with treating a lower volume of wastewater.

Methods used in Option B to reduce process wastewater discharge rates include recycle or reuse of the acid plant blowdown waste stream. As discussed in Section IX, the acid plant blowdown stream is composed of any process wastewater discharges resulting from or associated with the manufacture of by-product sulfuric acid at primary copper, primary lead, and primary zinc smelters. Any associated air pollution control or gas-conditioning systems for sulfur dioxide off-gases from pyrometallurgical operations at these plants (roasting, sintering, and converting) are also included as a constituent of the acid plant blowdown stream. Recycle of the acid plant blowdown is achieved through cooling towers or holding tanks.

OPTION C

Option C for the metallurgical acid plants subcategory consists of all control treatment requirements of Option B (lime precipitation. sedimentation, and in-process flow reduction) plus sulfide precipitation (followed by sedimentation), and multimedia filtration technology added at the end of the Option B treatment scheme. Sulfide precipitation is added to reduce cadmium, zinc, and other priority metal concentrations below concentrations achievable with lime and settle. For lead and zinc acid plants, sulfide precipitation and sedimentation is added after lime precipitation and sedimentation (see Figure X-3, page 1433). For one copper acid plant and all molybdenum acid plants, sulfide precipitation and pressure filtration are added before lime precipitation and sedimentation. Iron co-precipitation is also part of the technology basis for molybdenum acid plants. This technology is included to control discharges of molybdenum (see Figure X-4, page 1434).

Multimedia filtration is used to remove suspended solids, including precipitates of metals beyond the concentrations attainable by gravity sedimentation. The filter suggested is of the gravity, mixed media type, although other forms of filters, such as rapid sand filters or pressure filters, would perform satisfactorily.

INDUSTRY COST AND POLLUTANT REMOVAL ESTIMATES

As one means of evaluating each technology option, EPA developed estimates of the pollutant removal estimates and the compliance costs associated with each option. The methodologies are described below.

POLLUTANT REMOVAL ESTIMATES

A complete description of the methodology used to calculate the estimated pollutant removals achieved by the application of the various treatment options is presented in Section X of the General Development Document. The pollutant removal estimates have been revised from proposal based on comments and new data, however, the methodology for calculating pollutant removals was not changed. The data used for estimating pollutant removals are the same as those used to revise compliance costs.

Sampling data collected during the field sampling program were used to characterize the major waste streams considered for regulation. At each sampled facility, the sampling data were production normalized for each unit operation (i.e., mass of pollutant generated per mass of product manufactured). This value, referred to as the raw waste, was used to estimate the mass of toxic pollutants generated within the metallurgical acid plants subcategory. By multiplying the total subcategory production for a unit operation by the corresponding raw waste value, the mass of pollutant generated for that unit operation was estimated.

The volume of wastewater discharged after the application of each treatment option was estimated for each operation at each plant by comparing the actual discharge to the regulatory flow. The smaller of the two values was selected and summed with the other plant flows. The mass of pollutant discharged was then estimated by multiplying the achievable concentration values attainable with the option (mg/l) by the estimated volume of process wastewater discharged by the subcategory. The mass of pollutant removed is the difference between the estimated mass of pollutant generated within the subcategory and the mass of pollutant discharged after application of the treatment option. The pollutant removal estimates for the direct dischargers in the metallurgical acid plants subcategory are presented in Table X-1 (page 1429).

COMPLIANCE COSTS

Compliance costs presented at proposal were estimated using cost curves, which related the total costs associated with installation and operation of wastewater treatment technologies to plant process wastewater discharge. EPA applied these curves on a per plant basis, a plant's costs--both capital, and operating and maintenance--being determined by what treatment it has in place and by its individual process wastewater discharge (from dcp). The final step was to annualize the capital costs, and to sum the annualized capital costs, and the operating and maintenance costs, yielding the cost of compliance for the subcategory.

Since proposal, the cost estimation methodology has been changed as discussed in Section VIII of this supplement and in Section VIII of Vol. 1. A design model and plant-specific information were used to size a wastewater treatment system for each discharging facility. After completion of the design, capital and annual costs were estimated for each unit of the wastewater treatment system. Capital costs rely on vendor quotes, while annual costs were developed from the literature. The compliance costs for direct dischargers are presented in Table VIII-1 (page 1414).

BAT OPTION SELECTION - PROPOSAL

For proposal, EPA selected Option C (which includes lime precipitation, sedimentation, in-process flow reduction, and multimedia filtration) as the basis for BAT in the metallurgical acid plants subcategory.

Option F, which included reverse osmosis, is not demonstrated in the subcategory and is not clearly transferable from another subcategory or category and therefore was eliminated from consideration.

BAT OPTION SELECTION - PROMULGATION

The complete technology basis for this subcategory consists of in-process flow reduction through recycle and end-of-pipe lime and settle, sulfide precipitation (followed by sedimentation), and multimedia filtration technology for lead and zinc acid plants. For one copper acid plant and all molybdenum acid plants, the technology basis is in-process flow reduction, sulfide precipitation, pressure filtration, lime precipitation, sedimentation, and multimedia filtration. The technology basis for molybdenum acid plants also includes iron co-precipitation to control discharges of molybdenum.

Extensive self-monitoring data were submitted through the comments for the primary lead, primary zinc, primary copper, and metallurgical acid plant subcategories. The data were analyzed statistically for comparison with the combined metals data base. In addition, design and operating parameters for the treatment systems from which the data were collected was solicited through Section 308 authority. Of the seven plants submitting data, the Agency has determined that data from three of the plants should not be used to establish treatment because of design or operational deficiencies. However, three other plants may be well operated and, of these, the two primary zinc plants appear to have problems complying with the proposed zinc limitations (possibly due to high influent zinc concentrations or to ammonia interferences). The remaining plant, from the primary lead subcategory, appears to have difficulty meeting the proposed limit for cadmium. Although there were indications that the plants might not be operating their treatment systems optimally, the coefficient of variability for treated effluent was higher than for influent, and the influent was more variable than would be expected. The Agency as a conservative measure assumed that additional treatment (sulfide precipitation) is necessary to meet the proposed limits.

The last of the seven plants submitting data is from the primary copper subcategory and was found to be operating its treatment system at pH 12 to optimize arsenic removal. At pH 12, metals removal for pollutants other than arsenic decreases due to the increased solubility of metals at higher pH levels. Therefore, the Agency believes effluent data from this plant are not appropriate to determine treatment performance for other plants without this problem. After examining the arsenic values of the raw materials used by plants in the copper smelting subcategory, the Agency believes that this one plant is the only discharger experiencing arsenic concentrations frequently over 100 mg/l in the raw wastewater.

However, the Agency believes the addition of sulfide precipitation, in conjunction with multimedia filtration, will achieve the treatment performance values as proposed based on the lower solubility of metal sulfides (i.e., lower than metal hydroxides) as well as performance data for this technology on inorganic chemical wastewaters. (Sulfide precipitation technology is discussed fully in Section VII of Vol. 1.

Application of the promulgated BAT mass limitations will result in the removal of an estimated 145,000 kg/yr of priority pollutants generated. The final BAT effluent mass limitations will remove 2,120 kg/yr of priority metals over the intermediate BAT option considered, which lacks filtration. Both options are economically achievable. EPA believes that the incremental removal justifies selection of filtration as part of BAT model technology. Filtration is demonstrated at two metallurgical acid plant facilities, while sulfide precipitation is demonstrated at five plants in the nonferrous metals manufacturing category (phases I and II). The estimated capital investment cost of BAT is $2.5 million (March, 1982 dollars) and the estimated annual cost is $2.0 million.

FINAL AMENDMENTS TO THE REGULATION

After promulgation, petitioners questioned the data on which the treatment effectiveness concentration for molybdenum removal is based. As a part of a settlement agreement, the petitioners agreed to install iron coprecipitation, the model technology, on all of the molybdenum-bearing wastestreams at their facilities regulated under this subcategory and to provide operating data to the Agency. EPA agreed to consider these data in any rulemaking to propose new molybdenum limits. In the interim, EPA agreed to propose to suspend the molybdenum limitations in the previously promulgated BPT and BAT limitations, NSPS and PSNS for this subcategory. EPA would then recommend interim limits for use in permits on a Best Professional Judgment (BPJ) basis. Interim limits, based on a monthly average treatment effectiveness of 30 mg/l and a daily maximum of 60 mg/l, were established which will be effective until April 30, 1988. At that time, if no full-scale data are available, EPA will establish limits based on the results of a bench-scale iron coprecipitation data obtained under the supervision of the Agency.

WASTEWATER DISCHARGE RATES

As discussed in Section III, the principal wastewater sources in the metallurgical acid plant subcategory include acid plant scrubber blowdown, mist precipitation blowdown, box cooler blowdown, and mist elimination blowdown. These wastewater sources have been combined into a single wastewater stream, referred to as acid plant blowdown.

The proposed BAT discharge rate for metallurgical acid plant wastewater was 2,554 l/kkg (612.5 gallons/ton) of 100 percent sulfuric acid production capacity. This is the allowance promulgated for BAT. This value represents the best existing practices of the subcategory, as determined from the analysis of the dcps. Individual water use and discharge rates from the plants surveyed are presented in Section V of this supplement for the acid plant blowdown streams. At proposal, 20 of the 21 metallurgical acid plants for which dcp information was available reported an acid plant wastewater stream. Seven of these plants recycle greater than 86 percent of their acid plant wastewater. The BAT discharge rate was based on the average discharge rate of the plants with greater than 86 percent recycle (refer to Section VII of Vol. 1.) The plant with 100 percent recycle was not included in the average.

Revised discharge flows were submitted by two plants after proposal. These data supported the proposed flow allowance. The Agency received no data demonstrating that the proposed BAT flow allowance should be changed.

As part of the proposal, dcps were received from the three molybdenum acid plants. Data from these dcps were used to calculate production normalized flows for these plants. Because these flows are consistent with the rate promulgated for copper, lead, and zinc acid plants, the Agency decided not to revise the BAT discharge rate and to use this rate for molybdenum acid plants.

REGULATED POLLUTANT PARAMETERS

In implementing the terms of the Consent Agreement in NRDC v. Train, Op. Cit., and 33 U.S.C.c1314 (b)(2)(A and B) (1976), the Agency placed particular emphasis on the priority pollutants. The raw wastewater concentrations from individual operations and the subcategory as a whole were examined to select certain pollutants and pollutant parameters for consideration for limitation. This examination and evaluation, presented in Section VI, concluded that 13 pollutants and pollutant parameters are present in metallurgical acid plant wastewaters at concentrations that can be effectively reduced by identified treatment technologies. (Refer to Section VI.)

However, the cost associated with analysis for priority metal pollutants has prompted EPA to develop an alternative method for regulating and monitoring priority pollutant discharges from the nonferrous metals manufacturing category. Rather than developing specific mass effluent limitations and standards for each of the priority metals found in treatable concentrations in the raw wastewaters from a given subcategory, the Agency is promulgating effluent limitations only for those pollutants generated in the greatest quantities as shown by the pollutant removal estimate analysis. The Agency is promulgating effluent mass limitations to control the discharge of five priority metal pollutants present at all types of metallurgical acid plants. Since acid plants are operated in conjunction with primary lead, primary copper, primary molybdenum and primary zinc plants, the pollutants selected for limitation in those subcategories are selected for limitation in the metallurgical acid plants subcategory. Therefore, certain regulated pollutants may not be present at a specific acid plant. For example, arsenic may not be found at primary zinc acid plants, but mass limitations are established to control arsenic at primary copper acid plants. The pollutants selected for specific limitation are listed below:

115. arsenic
118. cadmium
120. copper
122. lead
128. zinc
fluoride (molybdenum acid plants only)
molybdenum (molybdenum acid plants only)

By establishing limitations and standards for certain toxic metal pollutants, dischargers are expected to attain the same degree of control over priority metal pollutants as they would have been required to achieve had all the priority metal pollutants been directly limited.

This approach is justified technically since the treatment effectiveness concentrations used for lime precipitation and sedimentation technology are based on optimized treatment for concomitant multiple metals removal. Thus, even though metals have somewhat different theoretical solubilities, they will be removed at very nearly the same rate in a lime precipitation and sedimentation treatment system operated for multiple metals removal. Filtration as part of the technology basis is likewise justified because this technology removes metals non-preferentially.

The priority metal pollutants arsenic, cadmium, copper, lead and zinc are specifically limited to ensure the control of the excluded priority metal pollutants. These pollutants are indicators of the performance of the treatment technology. Molybdenum is not considered to be an indicator pollutant and is specifically limited only at molybdenum acid plants.

The following priority pollutants are excluded from limitation on the basis that they are effectively controlled by the limitations developed for arsenic, cadmium, copper, lead and zinc:

114. antimony
119. chromium
123. mercury
124. nickel
125. selenium
126. silver

EFFLUENT LIMITATIONS

The concentrations achievable by application of the BAT are explained in Section VII of Vol. 1 and summarized there in Table VII-21. The molybdenum treatment effectiveness values in that table have been questioned by Petitioners and EPA has agreed in a settlement agreement to temporarily suspend the molybdenum limits pending the development of new data.

The achievable concentrations (both one day maximum and monthly average values) are multiplied by the BAT normalized discharge rate for acid plant blowdown, 2,554 l/kkg (612.5 gallons/ton), to calculate the mass of pollutant allowed to be discharged per mass of 100 percent sulfuric acid production capacity. As discussed in Section IV, 100 percent sulfuric acid capacity is used rather than actual production. Use of capacity results in a better correlation between the comparison of water usage rates when they are production normalized. The results of these calculations in milligrams of pollutant per kilogram of 100 percent sulfuric acid production capacity represent the BAT effluent limitations and are presented in Table X-2 (page 1430) for the metallurgical acid plant subcategory. Table X--2 also presents the discharge allowances which would have been established for the unregulated priority pollutants if they had been specifically regulated. This information may be used by permit writers when developing permits for combined wastes or when additional specific regulation of these pollutants should become appropriate.

Table X-1

POLLUTANT REMOVAL ESTIMATES FOR METALLURGICAL ACID PLANTS DIRECT DISCHARGERS

POLLUTANT	TOTAL RAW WASTE (kg/yr)	OPTION B DISCHARGED (kg/yr)	OPTION B REMOVED (kg/yr)	OPTION C DISCHARGED (kg/yr)	OPTION C REMOVED (kg/yr)
Arsenic	43,035.5	1,136.8	41,898.7	757.9	42,277.6
Cadmium	526.5	176.1	350.4	109.2	417.3
Chromium	107.8	107.8	0.0	107.8	0.0
Lead	6,610.1	267.5	6,342.7	178.3	6,431.8
Mercury	315.9	133.7	182.2	80.2	235.7
Nickel	866.2	866.2	0.0	490.4	375.8
Selenium	1,491.8	668.7	823.1	445.8	1,046.0
Silver	255.7	222.9	32.8	156.0	99.7
Copper	12,786.5	1,292.8	11,493.7	869.3	11,917.2
Zinc	74,462.8	735.6	73,727.2	512.7	73,950.1
TOTAL TOXIC METALS	140,458.8	5,608.1	134,850.7	3,707.6	136,751.2
TSS	438,753.7	26,748.0	412,005.7	5,795.4	432,958.3
TOTAL CONVENTIONALS	438,753.7	26,748.0	412,005.7	5,795.4	432,958.3
TOTAL POLLUTANTS	579,212.5	32,356.1	546,856.4	9,503.0	569,709.5
FLOW (l/yr)		2,229,000,000		2,229,000,000	

NOTE: TOTAL TOXIC METALS = Arsenic + Cadmium + Chromium + Lead + Mercury + Nickel + Selenium + Silver + Copper + Zinc
TOTAL CONVENTIONALS = TSS
TOTAL POLLUTANTS = Total Toxic Metals + Total Conventionals

OPTION B = Lime Precipitation, Sedimentation, and In-process Flow Reduction
OPTION C = Option B, plus Sulfide Precipitation and Pressure Filtration Preliminary Treatment, and Multimedia Filtration for One Copper Acid Plant
OPTION C = Option B, plus Sulfide Precipitation and Sedimentation, and Multimedia Filtration for Lead and Zinc Acid Plants

TABLE X-2

BAT MASS LIMITATIONS FOR THE METALLURGICAL ACID PLANTS SUBCATEGORY

Acid Plant Blowdown BAT

Pollutant or pollutant property	Maximum for any one day	Maximum for monthly average
mg/kg (lb/million lbs) of 100 percent equivalent sulfuric acid capacity		
Antimony	4.929	2.196
*Arsenic	3.550	1.583
*Cadmium	0.511	0.204
Chromium	0.945	0.383
*Copper	3.269	1.558
*Lead	0.715	0.332
Mercury	0.383	0.153
Nickel	1.405	0.945
Selenium	2.094	0.945
Silver	0.741	0.306
*Zinc	2.605	1.073
*Fluoride[1]	89.390	50.820
*Molybdenum[1]	Reserved	Reserved

*Regulated Pollutant

[1] For molybdenum acid plants only.

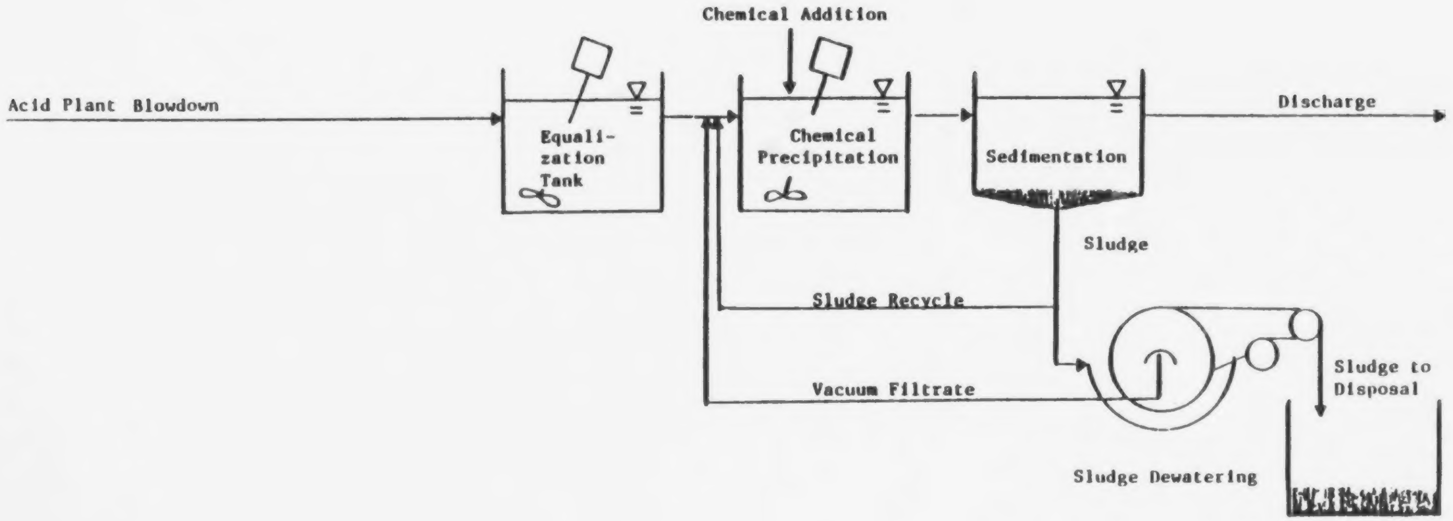
Chemical Addition
Acid Plant Blowdown
Equali-
zation
Tank
Chemical
Precipitation
Sedimentation
Discharge
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge to
Disposal
Sludge Dewatering

Figure X-1

BAT TREATMENT SCHEME OPTION A
METALLURGICAL ACID PLANT SUBCATEGORY

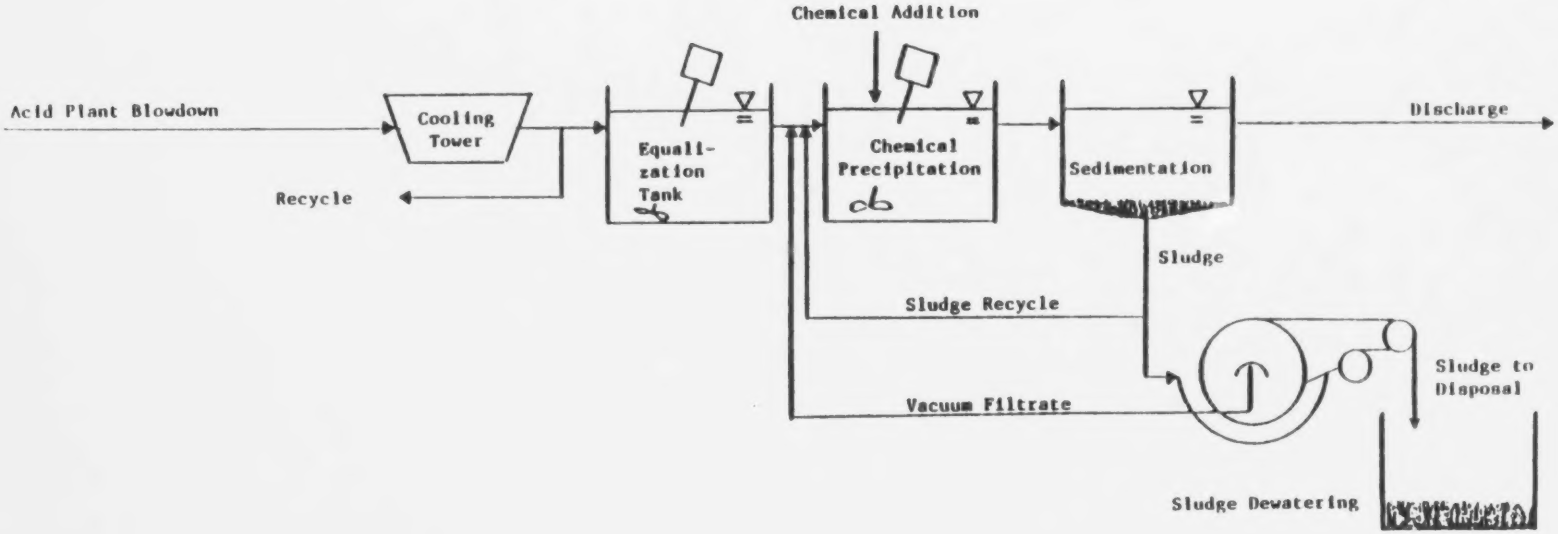
Acid Plant Blowdown
Cooling Tower
Recycle
Equalization Tank
Chemical Addition
Chemical Precipitation
Sedimentation
Discharge
Sludge
Sludge Recycle
Vacuum Filtrate
Sludge to Disposal
Sludge Dewatering

Figure X-2

BAT TREATMENT SCHEME OPTION B
METALLURGICAL ACID PLANT SUBCATEGORY

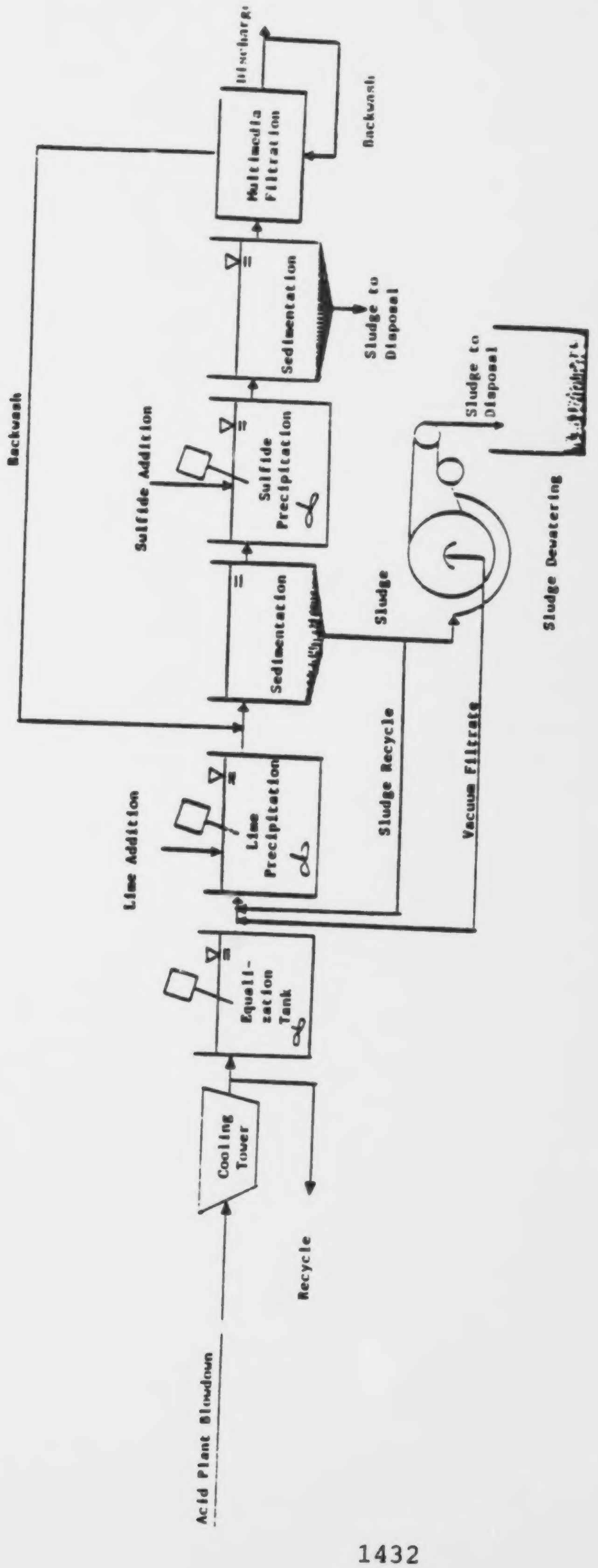
Acid Plant Blowdown
Recycle
Cooling Tower
Equali-zation Tank
Lime Addition
Lime Precipitation
Sludge Recycle
Vacuum Filtrate
Sedimentation
Sludge
Backwash
Sulfide Addition
Sulfide Precipitation
Sludge Dewatering
Sludge to Disposal
Sedimentation
Sludge to Disposal
Multimedia Filtration
Backwash
Discharge

Figure X-3

BAT TREATMENT SCHEME OPTION C FOR LEAD AND ZINC METALLURGICAL ACID PLANTS

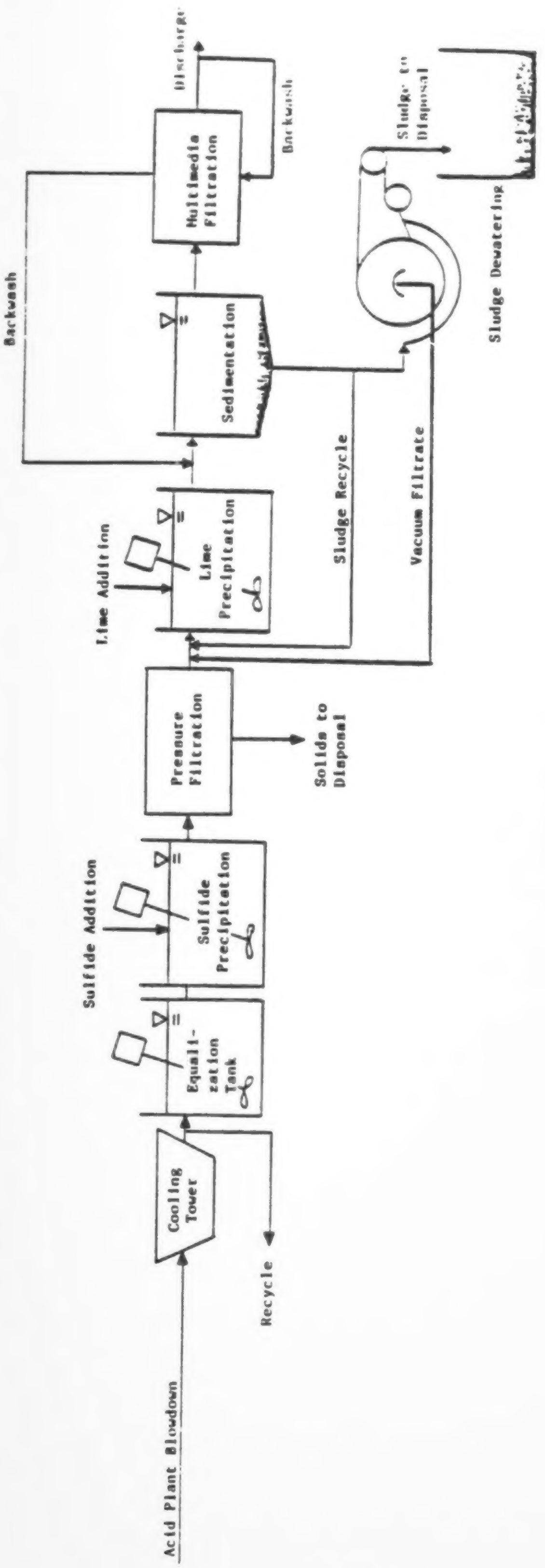
Acid Plant Blowdown
Cooling Tower
Recycle
Equalization Tank
Sulfide Addition
Sulfide Precipitation
Pressure Filtration
Solids to Disposal
Lime Addition
Lime Precipitation
Sludge Recycle
Vacuum Filtrate
Backwash
Sedimentation
Multimedia Filtration
Backwash
Discharge
Sludge to Disposal
Sludge Dewatering

Figure X-4

BAT TREATMENT SCHEME OPTION C FOR ONE PRIMARY COPPER METALLURGICAL ACID PLANT

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology (BDT). New plants have the opportunity to design the best and most efficient production processes and wastewater treatment technologies without facing the added costs and restrictions encountered in retrofitting an existing plant. Therefore, Congress directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible.

This section describes the technologies for treatment of wastewater from new sources, and presents mass discharge standards of regulated pollutants for NSPS based on the selected treatment technology.

TECHNICAL APPROACH TO BDT

All of the treatment technology options applicable to a new source were previously considered for the BAT options. Three options were considered for BDT for copper, lead, zinc, and molybdenum metallurgical acid plants. On March 18, 1985, the Agency published a Notice of Data Availability which revised these three options to include iron co-precipitation for molybdenum acid plants to control discharge of molybdenum. The options considered for BDT are identical to the BAT options discussed in Section X. In-process flow reduction required under Option B is based on a recycle ratio obtained by averaging discharge rates from plants that recycled 86 percent or more of their acid plant blowdown. The treatment technologies considered for BDT are:

OPTION A

- o Chemical precipitation and sedimentation
- o Iron co-precipitation for molybdenum acid plants

OPTION B

- o Chemical precipitation and sedimentation
- o In-process flow reduction
- o Iron co-precipitation for molybdenum acid plants

OPTION C

- o Chemical precipitation and sedimentation

- In-process flow reduction
- Sulfide precipitation (and sedimentation or pressure filtration)
- Iron co-precipitation for molybdenum acid plants
- Multimedia filtration

Partial or complete reuse or recycle of wastewater is an essential part of Options B and C. Reuse or recycle can precede or follow end-of-pipe treatment.

BDT OPTION SELECTION

EPA is promulgating that the best available demonstrated technology for the metallurgical acid plants subcategory be equal to BAT. The best demonstrated technology consists of lime precipitation, sedimentation, in-process flow reduction, sulfide precipitation, sedimentation or pressure filtration, iron coprecipitation for molybdenum acid plants, and multimedia filtration. EPA has not found that new plants could achieve any additional flow reduction beyond that proposed for BAT.

REGULATED POLLUTANT PARAMETERS

The Agency has no data that suggest that the pollutants found in treatable concentrations in processes within new sources will be any different than with existing sources. Accordingly, pollutants selected for specific limitation under NSPS, in accordance with the rationale of Sections VI and X, are identical to those selected for BAT. The conventional pollutant parameters TSS and pH are also selected for limitation.

NEW SOURCE PERFORMANCE STANDARDS

The promulgated NSPS discharge flow for acid plant blowdown is the same as the promulgated BAT discharge flow. See Section X for a discussion of the molybdenum treatment effectiveness value and effluent limitations. The acid plant blowdown discharge flow is 2,554 l/kkg (612 gallons/ton). The mass of pollutant allowed to be discharged per mass of product is calculated by multiplying the achievable treatment concentration (mg/l) by the normalized wastewater discharge flow (l/kkg). The BDT achievable treatment concentrations are identical to the BAT achievable treatment concentrations. New source performance standards, as determined from the above procedure are shown in Table Xl-1 (page 1437) for the acid plant blowdown stream.

TABLE XI-1

NSPS FOR THE METALLURGICAL ACID PLANT SUBCATEGORY

Acid Plant Blowdown NSPS

Pollutant or pollutant property	Maximum for any one day	Maximum for monthly average
mg/kg (lb/million lbs) of 100 percent equivalent sulfuric acid capacity		
Antimony	4.929	2.196
*Arsenic	3.550	1.583
*Cadmium	0.511	0.204
Chromium	0.945	0.383
*Copper	3.269	1.558
*Lead	0.715	0.332
Mercury	0.383	0.153
Nickel	1.405	0.945
Selenium	2 094	0.945
Silver	0.741	0.306
*Zinc	2.605	1.073
*Fluoride[1]	89.390	50.820
*Molybdenum[1]	Reserved	Reserved
*TSS	38.310	30.650
*pH	Within the range of 7.5 to 10.0 at all times	

*Regulated Pollutant

[1] For molybdenum acid plants only.

SECTION XII

PRETREATMENT STANDARDS

Section 307(b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES), which must be achieved within three years of promulgation. PSES are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of publicly owned treatment works (POTW). The Clean Water Act of 1977 requires pretreatment for pollutants, such as heavy metals, that limit POTW sludge management alternatives. Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect discharge facilities, like new direct discharge facilities, have the opportunity to incorporate the best available demonstrated technologies, including process changes, in-plant controls, and end-of-pipe treatment technologies, and to use plant site selection to ensure adequate treatment system installation. Pretreatment standards are to be technology-based, analogous to the best available technology for removal of toxic pollutants.

This section describes the control and treatment technologies for pretreatment of process wastewaters from existing sources and new sources in the metallurgical acid plant subcategories. Pretreatment standards for regulated pollutants are presented based on the selected control and treatment technology.

TECHNICAL APPROACH TO PRETREATMENT

Before proposing pretreatment standards, the Agency examines whether the pollutants discharged by the industry pass through the POTW or interfere with the POTW operation or its chosen sludge disposal practices. In determining whether pollutants pass through a well-operated POTW, achieving secondary treatment, the Agency compares the percentage of a pollutant removed by POTW with the percentage removed by direct dischargers applying the best available technology economically achievable. A pollutant is deemed to pass through the POTW when the average percentage removed nationwide by well-operated POTW meeting secondary treatment requirements, is less than the percentage removed by direct dischargers complying with BAT effluent limitations guidelines for that pollutant. (See generally, 46 Fed. Reg. at 9415-16 (January 28, 1981).)

This definition of pass through satisfies two competing objectives set by Congress: (1) that standards for indirect dischargers be equivalent to standards for direct dischargers, while at the same time, (2) that the treatment capability and performance of the POTW be recognized and taken into account in regulating the discharge of pollutants from indirect dischargers. The Agency compares percentage removal rather than the mass or

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concentration of pollutants discharged because the latter would not take into account the mass of pollutants discharged to the POTW from non-industrial sources nor the dilution of the pollutants in the POTW effluent to lower concentrations due to the addition of large amounts of non-industrial wastewater.

PRETREATMENT STANDARDS FOR EXISTING AND NEW SOURCES

Options for pretreatment of wastewaters are based on increasing the effectiveness of end-of-pipe treatment technologies. All inplant changes and applicable end-of-pipe treatment processes have been discussed previously in Sections X and XI. The treatment options for PSES and PSNS are the same as the options discussed in Section X. A description of each option is presented in Section X.

Treatment technologies used for the PSES and PSNS options are:

Option A

- Chemical precipitation and sedimentation
- Iron co-precipitation for molybdenum acid plants

Option B

- Chemical precipitation and sedimentation
- In-process flow reduction
- Iron co-precipitation for molybdenum acid plants

Option C

- Chemical precipitation and sedimentation
- In-process flow reduction
- Sulfide precipitation (and sedimentation or pressure filtration)
- Iron co-precipitation for molybdenum acid plants
- Multimedia filtration

INDUSTRY COST AND POLLUTANT REMOVAL ESTIMATES

The industry cost and pollutant removal estimates of each treatment option were used to determine the most cost-effective option. The methodology applied in calculating pollutant reduction benefits and plant compliance costs is discussed in Section X.

Table XII-1 (page 1443) shows the pollutant removal estimates for the one indirect discharger. Compliance costs are presented in Table VIII-2 (page 1414).

PSES AND PSNS OPTION SELECTION

EPA did not propose PSES for metallurgical acid plants in the proposed rulemaking for nonferrous metals manufacturing even though there is one existing indirect discharging metallurgical acid plant. At proposal, it was estimated that this plant currently discharged less pollutants than would be allowed under PSES because its wastewater discharge rate was much less than that allowed. The revised removal estimates, however, indicate that the PSES technology will remove 367 kg/yr of priority metals over current discharge estimates. The Agency has, therefore, decided to promulgate PSES for metallurgical acid plants.

EPA is promulgating PSES equal to BAT for this subcategory. Promulgation of PSES for the metallurgical acid plant subcategory will prevent pass-through of cadmium and zinc. The revised pollutant removal estimates indicate that PSES will remove 12,400 kg/yr of the priority metals generated. The final PSES limitations will remove 330 kg/yr priority pollutants over the intermediate option, which lacks filtration. Since both options are economically achievable and both prevent pass-through, the Agency is promulgating PSES equal to BAT. Implementation of the promulgated PSES will result in an estimated capital cost of $0.161 million (March, 1982 dollars) and an estimated annual cost of $0.085 million (March, 1982 dollars).

The technology basis for promulgated PSNS is identical to NSPS and BAT, which are based on lime precipitation, sedimentation, in-process flow reduction, sulfide precipitation and sedimentation, iron co-precipitation for molybdenum acid plants, and multimedia filtration. EPA has not identified any demonstrated technology that provides better pollutant removal than PSNS technology. The wastewater discharge rate for the acid plant blowdown stream is the same for PSNS and BAT. The Agency believes that no additional flow reduction is feasible for new sources because the only other flow reduction technology, reverse osmosis, is not demonstrated nor is it clearly transferable to the nonferrous metals manufacturing category.

REGULATED POLLUTANT PARAMETERS

The pollutants selected for limitation under PSES are cadmium and zinc. Since the one indirect discharging metallurgical acid plant is found at a primary zinc facility, only those pollutants associated with primary zinc were evaluated for pass-through. This analysis indicated that copper and lead would not pass through a well-operated POTW with secondary treatment. With PSES technology, it was estimated that 33 percent of the pollutants would be removed. A POTW, however, would remove 58 percent of the copper and 48 percent of the lead.

Metals may be toxic to the biological system, pass through largely untreated, or limit sludge management alternatives due to the metals that are removed with the sludge. PSES prevent the pass-through of cadmium and zinc.

Pollutants selected for limitation under PSNS, in accordance with the rationale of Sections VI and X, are identical to those selected for specific limitation for BAT. PSNS prevent the pass-through of arsenic, cadmium, copper, lead, zinc, molybdenum and fluoride.

PRETREATMENT STANDARDS

The PSES and PSNS discharge flow for acid plant blowdown is the same as the BAT discharge flow of 2,554 liters per metric ton (612.5 gallons/ton) of 100-percent sulfuric acid capacity. See Section X for a discussion of the molybdenum treatment effectiveness value and effluent limitation. The mass of pollutant allowed to be discharged per mass of product is calculated by multiplying the achievable treatment concentration (mg/l) by the normalized wastewater discharge flow (l/kkg). The PSES and PSNS achievable treatment concentrations are identical to BAT and NSPS achievable treatment concentrations and are presented in Table VII-21 of Vol. 1. Pretreatment standards for existing and new sources, as determined from the above procedure are shown in Tables X11-2 and XII-3 for the acid plant blowdown stream.

Mass-based standards are promulgated for the metallurgical acid plant subcategory to ensure that the standards are achieved by means of pollutant removal rather than by dilution. They are particularly important since the standards are based upon flow reduction; pollutant limitations associated with flow reduction cannot be measured by any other way but as a reduction of mass discharged.

Table XII-1

POLLUTANT REMOVAL ESTIMATES FOR METALLURGICAL ACID PLANTS INDIRECT DISCHARGERS

POLLUTANT	TOTAL RAW WASTE (kg/yr)	OPTION B DISCHARGED (kg/yr)	OPTION B REMOVED (kg/yr)	OPTION C DISCHARGED (kg/yr)	OPTION C REMOVED (kg/yr)
Arsenic	3,893.0	78.4	3,814.6	52.3	3,840.8
Cadmium	47.6	47.6	0.0	7.5	40.1
Chromium	9.8	9.8	0.0	9.8	0.0
Lead	598.0	18.4	579.5	12.3	585.7
Mercury	28.6	9.2	19.4	5.5	23.0
Nickel	78.4	78.4	0.0	33.8	44.5
Selenium	134.9	46.1	88.8	30.7	104.2
Silver	23.1	15.4	7.8	10.8	12.4
Copper	1,156.7	89.1	1,067.5	59.9	1,096.7
Zinc	6,736.0	199.8	6,536.2	35.4	6,700.6
TOTAL TOXIC METALS	12,706.0	592.2	12,113.8	258.0	12,448.0
TSS	39,690.0	1,844.4	37,845.6	399.6	39,290.4
TOTAL CONVENTIONALS	39,690.0	1,844.4	37,845.6	399.6	39,290.4
TOTAL POLLUTANTS	52,396.0	2,436.6	49,959.4	657.6	51,738.4
FLOW (l/yr)		153,700,000		153,700,000	

NOTE: TOTAL TOXIC METALS = Arsenic + Cadmium + Chromium + Lead + Mercury + Nickel + Selenium + Silver + Copper + Zinc

TOTAL CONVENTIONALS = TSS

TOTAL POLLUTANTS = Total Toxic Metals + Total Conventionals

OPTION B = Lime Precipitation, Sedimentation, and In-process Flow Reduction

OPTION C = Option B, plus Sulfide Precipitation and Pressure Filtration Preliminary Treatment, and Multimedia Filtration for One Copper Acid Plant

OPTION C = Option B, plus Sulfide Precipitation and Sedimentation, and Multimedia Filtration for Lead and Zinc Acid Plants

TABLE XII-2

PSES FOR THE METALLURGICAL ACID PLANT SUBCATEGORY

Acid Plant Blowdown PSES

Pollutant or Pollutant Property	Maximum for Any One Day	Maximum for Monthly Average
mg/kg (lbs/million lbs) of 100 percent sulfuric acid capacity		
Cadmium	0.511	0.204
Zinc	2.605	1.073

TABLE XII-3

PSNS FOR THE METALLURGICAL ACID PLANT SUBCATEGORY

Acid Plant Blowdown PSNS

Pollutant or pollutant property	Maximum for any one day	Maximum for monthly average
mg/kg (lb/million lbs) of 100 percent equivalent sulfuric acid capacity		
Antimony	4.929	2.196
*Arsenic	3.550	1.583
*Cadmium	0.511	0.204
Chromium	0.945	0.383
*Copper	3.269	1.558
*Lead	0.715	0.332
Mercury	0.383	0.153
Nickel	1.405	0.945
Selenium	2.094	0.945
Silver	0.741	0.306
*Zinc	2.605	1.073
*Fluoride[1]	89.390	50.820
*Molybdenum[1]	Reserved	Reserved

*Regulated Pollutant

[1] For molybdenum acid plants only.

SECTION XIII

BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY

EPA is not promulgating best conventional pollutant control technology (BCT) for the metallurgical acid plants at this time.

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